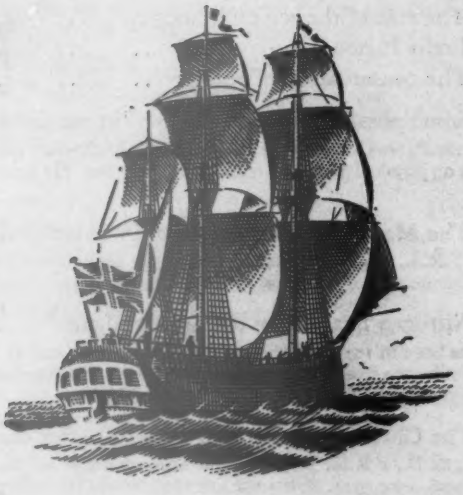
ENDEAVOUR

A quarterly review designed to record the progress of the sciences in the service of mankind



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ENDEAVOUR

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The centenary of anaesthesia

It is impossible to assign the discovery of anaesthesia to any one person or to any one date, but so many events of fundamental importance in the history of anaesthetics occurred about a hundred years ago that the centenary of anaesthesia may rightly be commemorated at this time. In this connection it is appropriate to remember that, although anaesthetics are used almost exclusively by the medical and dental professions, their discovery and development owe much to the work of the pure scientist. The entire history of anaesthesia is, in fact, an illustration of the fruitful results of close collaboration between physicians and scientists.

Two outstandingly important dates in the history of anaesthesia are 16th October, 1846, when William Thomas Green Morton successfully demonstrated anaesthesia with ether before a gathering of surgeons at Boston, Massachusetts, and 4th November, 1847, when James Young Simpson and Drs Keith and Matthews Duncan recovered their senses underneath Simpson's dining-room table after testing chloroform, a drug 'far better and stronger than ether.' Chloroform and ether remained pre-eminent in surgical anaesthesia for decades, and both, despite the development and acceptance of many others, are still widely employed. These two events represented the culmination of earlier research by workers who, though they failed to achieve the goal of establishing anaesthesia in general medical practice, went far along the road towards it.

The first discovery of direct preliminary importance was the isolation of oxygen by Priestley in 1774. The physiological significance of the new gas was quickly appreciated by Lavoisier, who in the period 1774–85 elucidated the composition of the atmosphere and established the main principles of the respiratory process. These discoveries led to the development of pneumatic medicine, which concerned itself with the treatment of disease by the inhalation of gases. A noteworthy pioneer in pneumatic medicine was Thomas Beddoes, a lecturer in chemistry at Oxford. In 1794 he established the Pneumatic Institution at Clifton, Bristol, in order to pursue his investigations. One of the substances Beddoes studied was 'sulphuric ether,' the vapour of which he found to be of value in treating pains in the chest. Among those whom Beddoes attracted to Bristol was the young Humphry Davy. When Davy became superintendent of the Pneumatic Institute he was scarcely twenty years of age, but his enthusiasm for chemistry outweighed his youthful inexperience. One of his first tasks was to investigate the chemical and physiological properties of nitrous oxide, and in April 1799 he discovered that this gas was not only respirable but that, when respired, it produced a state of intoxication in which pain was deadened. He recognized the potential value of the gas in surgery, for in 1800 he wrote: 'nitrous oxide . . . appears capable of destroying physical pain, (and) it may probably be used with advantage during surgical operations in which no great effusion of blood takes place.' Unfortunately Davy himself made little effort to press this claim, so that the medical profession did not investigate it until many years later. Davy had, however, noticed another quality of nitrous oxide, namely its power of inducing a curious hilarity, which earned for it the name of 'laughing gas.' So pleasurable was the sensation that laughing-gas parties became popular in the early nineteenth century. It was owing to this frivolous application that the gas remained familiar and, nearly fifty years after Davy's original observations, eventually found its rightful place among surgical anaesthetics. In 1818 it was suggested, possibly by Michael Faraday, that ether vapour would produce the same kind of hilarity

as nitrous oxide, and very soon ether too was inhaled at fashionable parties.

At about this time a British physician named Henry Hill Hickman, who practised in Shropshire, found that surgical operations could be painlessly performed on animals after causing them to inhale carbon dioxide. He published his results in 1824, but in the absence of any support from professional colleagues did not attempt to apply his method to human beings.

Meanwhile the fashion of laughing gas and ether frolics had spread to the United States. In the course of one of them C. W. Long, a physician of Georgia, observed that while under the influence of ether his guests often bruised themselves quite severely without feeling pain. In the period 1842–4 he successfully used ether anaesthesia for several minor surgical operations. In December 1844 a Connecticut dentist, Horace Wells, attended a nitrous oxide party and made the same observation as Long had done at the ether party. Next day he induced a colleague to extract one of his teeth for him after he had inhaled nitrous oxide. Wells felt no pain, and thenceforth used nitrous oxide anaesthesia in his dental practice. Unfortunately, when Wells and his fellow dentist Morton gave a public demonstration in Boston it was a failure, and his method was discredited. Morton was not discouraged, however, and determined to try ether vapour in place of nitrous oxide. On the advice of a chemical friend, C. T. Jackson, Morton procured a very pure sample of ether and used this successfully during the extraction of a tooth. On 16th October, 1846, Morton gave his now famous demonstration of the use of ether anaesthesia in surgery before a medical and scientific audience at Boston. This demonstration was a complete success. The sceptics were convinced, and the principle of ether anaesthesia was quickly accepted by the medical profession in the United States, in England, in France, and then throughout the world.

Thirteen months later James Young Simpson, seeking a more tractable substance than ether, successfully demonstrated in Edinburgh the valuable anaesthetic qualities of chloroform. Although this agent was soon found to be more dangerous than ether, the more precise control with which it could be administered soon made it the more popular of the two.

For many years the development of anaesthesia was confined to the perfection of techniques for administering chloroform, ether, and nitrous oxide. In 1884, however, a great step forward was made when Carl Koller introduced cocaine into ophthalmic surgery and this laid the foundation of the modern technique of local anaesthesia. In doing so he was in a sense reverting to a very old method, for such drugs as opium and mandragora were well known to the ancients as analgesics, and formed part of the normal equipment of physicians. Their use was, however, hazardous, owing to the absence of methods of standardization. Koller revived interest in substances of this kind at a time when medical and scientific knowledge was sufficiently developed to permit their use with comparative safety.

Chemists in particular quickly recognized the opportunities presented by the need for new and better anaesthetics. From investigation of the structures of natural substances such as cocaine and morphine they quickly turned to the synthesis of drugs unknown in nature, modelling them first on the natural products and later investigating totally new classes of compounds. In consequence the physician's choice of anaesthetics multiplied itself with almost bewildering rapidity. Ether, chloroform, and nitrous oxide remain in general use, but to them now must be added such substances as ethyl chloride, vinyl ether (vinesthene), trichlorethylene (trilene), cyclopropane, pentothal, kemithan, procaine, and nupercaine.

The use of anaesthetics in surgery was rightly described by Sir William Osler as the greatest single discovery in the history of medicine, and the contribution it has made, and is yet to make, to the relief of human suffering is immeasurable. At a time when the destructiveness of applied science tends to obscure its far greater services to human welfare, scientists may well pride themselves on their share both in the discovery and in the effective development of surgical anaesthesia.

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The influence of man on marine life

C. M. YONGE

Man's direct influence on marine life is of comparatively recent origin, for until about two hundred years ago the amount of fishing and whaling that was carried on was too small to upset the equilibrium of nature. With improved ships, apparatus, and technique, however, came a vast and indiscriminate slaughter of marine life, and some species were exterminated altogether. There is now a general realization that wise cultivation of the sea is as necessary as wise cultivation of the land. Professor Yonge gives a broad survey of the problem.

Man has had a profound effect on terrestrial life. Hunting, first with flint tools and eventually with precise weapons, led to the extinction, for instance, of the bear, wolf, and boar in Britain and to the almost complete extinction of the bison of North America. Like the big game of Africa, this animal has been saved only by tardy methods of conservation. Fur-bearing animals have been remorselessly trapped. The faunae of the earth have been irreparably impoverished by the senseless destruction of unique birds such as the dodo and the great auk. Cultivation of crops and domestication of animals modified plants and animals so greatly that the exact origin of some is now obscure, and also effected far-reaching changes in the balance of nature. The greater the crops, the more the pests—insects, rodents, and birds especially—that were attracted.

With the full discovery of the world by western man, his crops and domestic animals were introduced into the new lands of America, Africa, and Australasia, and many of the foreign plants were brought back—accompanied all too frequently by foreign pests. Often for sentimental reasons, hosts of other plants and animals were similarly transported. This indiscriminate mixing of fauna and of flora led to disasters such as the plague of rabbits and of prickly pear in Australia, and that of bramble thickets spread by the introduction of the starling into New Zealand. Man, in despair, turned to nature to redress the balance he had wantonly destroyed, and, after some failures, there were developed methods of biological control which today are clearing the prickly pear from Australia and destroying the aphid pests of Californian orchards. But, despite the rigorous care enforced by bitter experience, the spread of life continues. The chance introduction of a malaria-carrying mosquito, *Anopheles gambiae*, from West Africa into Brazil in 1930 caused a terrible epidemic, overcome only after heroic measures by the Rockefeller Foundation.

Life in the sea has been much less affected by man. In the obscurity of its depths and in the breadth of its oceans animals are difficult to hunt to extinction, while most of the marine vegetation and the bulk of the diverse invertebrate fauna are useless to man. In the sea, it has been said, man reaps without sowing, and this is largely true. It follows that in this case the responsibility of ownership which came with the domestication of animals and the care of crops has rarely displaced the unconsidered greed of the hunter. This is nowhere better shown than in man's pursuit of the marine mammals.

There are three groups of these: the sirenia or sea cows, the marine carnivora such as seals and walruses, and the cetacea comprising the whales, dolphins, and porpoises. The sirenia are a small group of obscure origin and grotesque form. They inhabit inshore and estuarine waters, feeding on marine vegetation. They consisted, until recently, of three groups, the Indo-Pacific dugong, the manatee of the tropical Atlantic, and the much larger northern sea cow of the North Pacific. The first two survive, although actively hunted—fortunately mainly by native tribes—for their flesh and blubber. The sea cow became extinct some thirty years after its discovery in 1741 by the young German naturalist Georg Steller, who accompanied Behring's pioneer voyage to the North Pacific. Under the greatest difficulties, while marooned with unwilling helpers on Behring Island, he dissected and described the animal. The Russian hunters and traders who followed Behring quickly exterminated it, and, apart from Steller's description, there remain for study only a few skeletons. The destruction of the sea cow is the greatest blow yet dealt by man to the marine fauna, equivalent to that of the equally remarkable, harmless, and locally distributed dodo.

The walrus once occurred in vast numbers throughout the north Pacific and the Atlantic, where it extended as far south as Nova Scotia and

occasionally reached the shores of Britain. Following wholesale slaughter, such as that of 900 in one day near Spitsbergen in 1852 and that indicated by an annual import of 12,000 tusks into San Francisco alone between 1870 and 1880, it has become restricted to far northern waters. Many seals have suffered similar destruction, in particular those that breed in rookeries, like the Atlantic grey seal, and also the Greenland seal, which is the most important animal in the Newfoundland seal fishery, and the immense elephant seals (figure 1). Of these, the Californian species is now rare, but the naturalists of the *Discovery* Expedition found that the Antarctic species, which had been hunted on such a scale that it was reported virtually extinct a century ago, has reached a population of some 100,000 around South Georgia, where hunting is now annually confined to definite regions of the coast. A warm-water seal, once widely hunted in the West Indies, is now extremely rare.

These animals are sought for their blubber and flesh, but the eared seals, or sea lions, include the fur seals as much prized for their pelts as are sable, beaver, or silver fox on land. Formerly, various species abounded in northern and southern waters, but in the latter they have been almost exterminated, although there is some hope that they may be re-established in South Georgia. The greatest fishery of all was on the Pribilov Islands in the Behring Sea, some three hundred miles from Alaska. These islands were discovered by the Russians in 1786. There the vast rookery, with each huge bull gathering a harem sometimes exceeding one hundred females, and continuously fighting intruding males, must have presented an amazing spectacle. At the hands of Russian and American sealers upwards of two million seals were killed in fifty years. When the United States acquired the islands in 1867, attempts to control pelagic (open water) sealing in the Behring Sea led to international complications, and so to arbitration by a tribunal in Paris. This was followed by two Anglo-American commissions sent to the Pribilov Islands in 1891 and 1896–7. Eventually, pelagic sealing was prohibited by international agreement, and killing on the islands was restricted to the needs for food of the local population. Gradually the seal population recovered, and by confining hunting to the males, one bull to forty bearing cows being adequate for breeding, a rational control has been achieved.

It was the Russians also who discovered the delightful sea otter on the coast of Siberia. This rarest and most valuable of fur-bearing animals was hunted ruthlessly from there across the Aleutian Islands and south to California, where British and American hunters were at work. Almost complete extinction was again followed by international protection early in this century. Subsequent recovery has been slow, but populations of some two thousand in northern regions, and two hundred in southern, were estimated in 1939.

Helpless exposure on or near land invited slaughter of sea cows, seals, and sea otters. A similar fate has befallen the cetaceans, which include the largest animals ever to be evolved—the blue and fin whales—and which are so superbly adapted for aquatic life that they are even born in the sea. The tragic story of their ruthless hunting by man, which was begun by the Basques in the tenth century and has culminated in mass destruction by whale chasers operating from great factory ships in the Antarctic, has recently been related in ENDEAVOUR[1] and need not be retold.

Man the hunter has thus inflicted terrible loss on the marine mammals; fortunately it has not been worth his while, except in the one instance of the sea cow, to hunt them to final extinction. He has also, with the elaboration of increasingly efficient instruments of capture, made grave inroads into the stock of many of the more important food fishes. Here attention must be confined to the history of the European fishing grounds, in the exploitation of which Britain has played a leading part. The growth of the modern trawling industry dates from that of big industrial towns and the establishment of rapid transport between them and the fishing ports. The first North Sea trawlers came from Brixham in Devon. Originally in open boats, and later in two-masted smacks, the fishermen gradually extended their activities as far as the rich Dogger Bank. Towards the end of the last century steam trawlers employing the highly efficient otter trawl began to replace the sailing vessels, and to range as far north as the Barents Sea and as far south as Morocco. This wider range was necessary because the fish became increasingly fewer and smaller on the original grounds. Evidence of overfishing was given before a series of royal commissions but no action was taken, the extension of fishing to new areas tending to obscure the effects of depletion. Then came the war of 1914–18, which imposed a close season on fishing. The result after the war was striking: fish had

[1] L. Harrison Matthews, ENDEAVOUR, July 1946, p. 116.

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FIGURE 1 – *A herd of elephant seals on a beach in South Georgia. The figure of the sealer shows the size of the bull.*
(*Reproduced by courtesy of Dr L. Harrison Matthews.*)

FIGURE 2 – *Japanese oysters* (Ostrea gigas) *in Ladysmith Bay, Vancouver Island, where they flourish after transplantation from Japan.*

FIGURE 3 – *The moat, Fort Jefferson, Tortugas Islands, Gulf of Mexico.*

FIGURE 5 – *Zuider Zee dyke.*
Before this dyke was completed in 1932 a thorough ecological survey was made region enclosed by it. Subsequent changes in both the environment and the populatio been closely followed. The results of this conversion of a wide area of saline water inland lake have proved of great theoretical and practical importance.

FIGURE 4 (*left*) – *Starfish collected by tangles from American oyster bed.*

increased in both numbers and size. In the period between the wars much of the scientific activity of the Ministry of Fisheries was devoted to working out and testing possible remedies for overfishing. This was the more necessary because as the years passed the effects of overfishing again became obvious. To take but one example of many cited by Dr E. S. Russell in his book *The Overfishing Problem*: the landings of haddock per day's fishing by English steam trawlers in the North Sea were 7·8 cwt. in 1906; this fell to 4·6 cwt. in 1914, rose to 15·8 in 1919, and had descended again to only 2·6 cwt. in 1937 (figure 6).

One obvious method of control is to enlarge the mesh of the vast trawl nets which annually sweep over practically the entire productive surface of the fishing grounds. This would enable the smaller fish to escape for further growth, and possibly reproduction, before capture. Another, more far-reaching, measure is to limit fishing. This demands a wide knowledge of the natural reproductivity of the fish. Unlike the marine mammals, with their annual or biennial production of one calf, fish produce vast numbers of eggs annually, of which only a few reach maturity. Food, though abundant, is not infinite, and growth is checked owing to intense competition. In other words, a certain degree of fishing is definitely helpful. It reduces competition and enables more fish to attain a large size. But clearly too intensive fishing has the reverse effect. It is a question of knowing exactly how much can be taken out with safety, so that man may obtain a rich harvest without adversely affecting natural stocks. It is actually not only more economical to fish with fewer vessels but the yield may in fact be greater than if too many are employed and the effects of overfishing produced.

Despite the size and obscurity of the fishing grounds, the basic facts concerning the productivity of the chief north Atlantic food fishes are known. This is due to the labours of the scientific staffs of the English and Scottish fishery services and those of the other maritime countries of western Europe. All normally work in close co-operation through the International Council for the Exploration of the Sea. It is now possible to formulate measures of control which, when aided

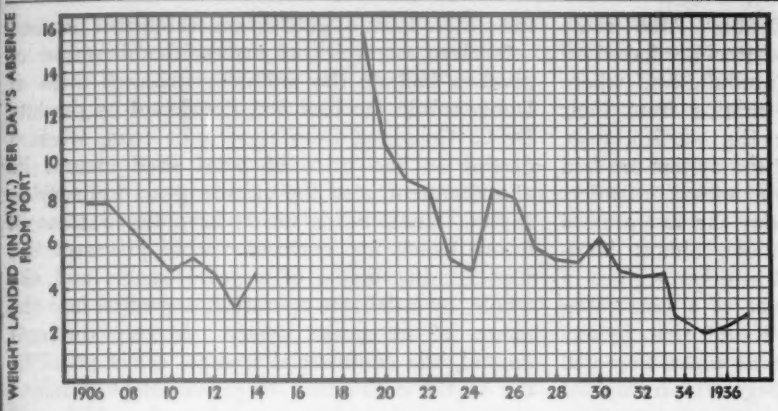


FIGURE 6 – *Graph showing weight (in cwt.) of haddock landed per day's absence by English steam trawlers in the North Sea. The effect of overfishing before and after the* 1914–18 *war, marked by the break in the graph, is well shown.*
(*Data from* The Overfishing Problem, *by E. S. Russell.*)

by continuous scientific supervision, will permit a rational exploitation of the fishing grounds. How successful such action may be is well shown by the result of treaties made between the United States and Canada in 1924 and 1930, and renewed in 1937, for the control of the Pacific halibut fishery, in which both countries are interested. An international fisheries commission was set up, and the fishery, which had undergone catastrophic decline, has recovered to a striking extent after limitation of fishing. In such rapid recovery we see the result of the great fecundity of fish. Populations of whales or seals may take a century to recover fully after too intensive hunting; those of fish will recover in a much shorter time.

Today, after the second close season imposed by war within a generation, there is clearly an opportunity for conserving the now well-stocked fishing grounds of western Europe. The British Government is certainly of this opinion. At its invitation an international overfishing conference was held in London not long after the end of the war. Representatives of all the maritime nations of western Europe except Germany attended, and considered the possibility of agreeing on measures for regulating fishing in the North Sea and adjacent areas. With the needs of starving populations constantly in mind far-reaching decisions could hardly be expected, but agreement was reached on an increase in the size of the mesh of trawl nets and also on size limits for the twelve most important bottom-living food fishes. Limitation of the tonnage of the fishing-fleets of the different countries, which was proposed by Great Britain, was not accepted, but the reality of the problem of overfishing was realized to the extent that an advisory committee was appointed to study the matter and propose suitable regulations for the prevention of overfishing in the North Sea and adjacent areas. There is thus some real ground for hope that in the future the fisheries of Europe may, like those of the north Pacific, pass from an era of over-reaching greed to one of rational exploitation based on conservation of the stocks.

Aquiculture, or the cultivation of aquatic life, has been conducted on a very limited scale compared with agriculture. With the exception of some cultivation in Japan of seaweeds from which agar is obtained, it is, moreover, restricted to animals. Its greatest, and by no means negligible, triumph has lain in the cultivation of oysters and other bivalves.

The aim of aquiculture is to increase some part of the population, either in numbers or in size of individuals. This may be done by improving their chances of survival, by transplanting them to regions where food is more abundant, or by increasing the fertility of confined waters. Although there is evidence that the Romans practised crude methods of oyster cultivation in Lake Fusaro and elsewhere, modern cultivation may be said to date from the work of Costé on the French oyster beds. These one-time prolific areas became progressively more depleted as a result of increasing demands from the growing industrial cities during the middle of the last century. Costé realized the fundamental fact that the oyster produces immense numbers of free-swimming larvae, but that only a minute fraction of these find the requisite clean, hard surface for settlement when they sink to the bottom. From his suggestions and experiments arose the modern method of putting out 'collectors,' consisting of half-cylindrical roofing tiles encrusted with lime and sand, in the early summer, when the oysters are ready to spawn. In this way millions of oyster 'spat' find surface for settlement. Costé further

realized the need for protection. After some months of growth, the young oysters are flaked off the tiles and transferred to 'ambulances,' where they are protected by wire netting from their numerous enemies such as crabs, starfish, rays, and marine snails. Later still the oysters are laid out on extensive parks, from which intruders are removed at low tide. Today the vast area of these parks around the shallow, almost land-locked bay of Arcachon, and in other regions of the French coast, are evidence of a flourishing industry. The French also found that oysters would grow and 'fatten' in areas where they will not necessarily breed, and began to transplant oysters into shallow lagoons or 'claires,' particularly around Marennes. In these warm waters the microscopic suspended plant life, or phytoplankton, on which the oysters feed increases rapidly. By such methods a highly organized and immensely productive oyster industry has been built up along the Atlantic coasts of France.

Similar methods, involving provision of settling surface, removal of pests, and transplantation to better feeding grounds, have been developed in many other countries, especially the United States. In the Delaware River, for instance, a natural breeding area some distance up the estuary is maintained, and a collecting surface, in this case consisting of masses of clean oyster shells spread loose or in wire-netting bags, is provided. These shells are later dredged up, the young oysters separated, and a proportion laid on planting beds nearer the sea, where they rapidly grow. The beds are regularly swept with wide-spreading cotton tangles (figure 4) in which the invading starfish are collected in millions, while continuous warfare is waged against other pests. The output of this one oyster fishery runs into some four hundred millions annually.

Along stretches of the Atlantic coast the French also cultivate mussels on long fences of piles and wattling driven into the mud flats. This *bouchot* system was introduced by an Irishman named Walton, who was the sole survivor from a small vessel wrecked in 1235 in the Anse de l'Aiguillon. On the muddy shores of this shallow bay, widely exposed at low tide, he is said to have driven stakes for the attachment of roughly woven grass nets in which he hoped to snare sea birds. He soon found that his nets became covered with mussels, which grew much larger than those on the shore and which proved an excellent source of food. He then took to planting stakes with interwoven twigs between them and so established the simple form of cultivation which still persists.

Modern examples of successful cultivation of bivalves include the unique pearl shell farm at Dongonab in the Red Sea, developed by the late Dr C. Crossland from 1905 until 1923, when a decline in the price of pearl shell caused its abandonment, and the culture pearl industry in Japan. Small beads which form the nucleus of future pearls are enclosed within pieces of the shell-forming tissues of a pearl oyster, and the whole, by a delicate operation, is grafted into the tissues of an intact oyster. A very different animal, the commercial sponge, offers possibilities to the cultivator. It grows attached like a plant, and cuttings may be made which will round off and grow under suitable conditions.

Transplantation of marine animals over great distances raises much greater problems than does that of terrestrial animals. If climate and food are suitable, many domestic and other animals may flourish in the southern hemisphere or in North America as well as, or even better than, they did in their original home in the Old World. Fresh-water fishes may also be transported successfully, as the teeming populations of trout and other fish introduced into the rivers and lakes of New Zealand bear witness. But with marine fish there is the additional factor of spawning migrations. In general, fish grow on their feeding grounds but then migrate against the prevailing currents to spawning areas characterized by very sharply defined physical and chemical conditions. From these the small, surface-dwelling larvae are carried passively back by the currents to the adult feeding grounds, sometimes by way of 'nursery' areas. Thus, though an adult fish may feed and grow in new surroundings, the whole complex mechanism of spawning migrations is upset, and the animals fail to establish themselves. Attempts to introduce herring into New Zealand waters failed probably for this reason. Atlantic salmon, successfully introduced into the rivers, apparently failed to find their way back to the rivers where they must spawn after feeding and growing in the sea.

On the other hand, transplantation over limited distances is possible. Marked plaice have been transplanted from coastal waters to the rich feeding grounds of the Dogger Bank and have there grown much faster than similar animals on the original grounds. The Danes have successfully transplanted small plaice from the crowded waters of the North Sea to the richer feeding grounds of the Limfjord.

It is also possible to transplant some marine

invertebrates which live and spawn in the same place, usually in shallow water. Oysters and other bivalves are normally 'relayed' on a large scale, although attempts to establish lobsters, which have a more complicated life-history, into New Zealand waters have failed. In Great Britain, where the population of 'native' oysters has greatly declined, young or 'seed' oysters have been purchased from France or the United States. Some of those from France have been of the same species as the 'native,' *Ostrea edulis*, but many have been Portuguese oysters, *O. angulata*, which colonized the southern parts of the French Atlantic coast during the past half-century. This oyster grows well on British beds but never spawns, and so can never become established here. It is indeed the spawning temperature, rather than the temperature at which the adult can live, that largely controls the distribution of marine invertebrates. *Ostrea edulis* spawns when the temperature reaches about 15° C, but *O. angulata* does not spawn until 20° C, which is not attained round our coasts. The same difficulty was found when the Japanese oyster, *O. gigas*, was introduced along the Pacific coasts of North America to replace the smaller local species. The temperature is rarely high enough to permit natural spawning, but some success was achieved in the summer months by placing the oysters in floats where the water reached a higher temperature than on the bottom. Later, successful use was made of discoveries by Dr P. S. Galtsoff of the United States Bureau of Fisheries, who found that oysters will breed at lower temperatures if stimulated by the presence of their own genital products in the water. In Vancouver, the Japanese oyster (figure 2) has been regularly induced to spawn by pouring suspensions of ripe egg and sperm, obtained from the sheds where oysters are opened and canned, over the beds at the height of the summer.

So far as we have discussed it, cultivation in the sea consists of ensuring high survival rate of certain stocks in areas where food is abundant. Increase in available food, as produced on land by the use of fertilizers, is still in the experimental stage in aquiculture. The 'fattening' of oysters in the *claires* at Marennes is due to the enrichment of the water by seepage of nutrient salts from the land, the rich microscopic flora so ensured forming food for the oysters. In limited masses of water, fertilization by addition of nutrient salts containing available nitrogen and phosphorus is feasible, and initial experiments by Norwegian and Danish biologists have revealed significant increases in plant and animal life. Similar experiments, aimed at an eventual enrichment of the local stocks of fish, have been carried out during recent years in small lochs along the west coast of Scotland.

The dispersal of the fauna of the land by the activities of man is in no way paralleled in the sea. Some of the reasons for this, such as the association of breeding migrations in fish with ocean currents, and the influence of temperature on the breeding of many marine animals, have been noted. Nevertheless species have been carried to new areas either deliberately, as in the case of the oysters, or else accidentally. When American oysters were relaid on British beds they were accompanied by the slipper limpet, *Crepidula*. This was first noted in the eighties of last century and now extends from the Humber round the south coast as far as Dorset. Unlike the species of oyster which it accompanied here, it is able to breed within the range of temperature found around our coasts and has firmly established itself. It is now a major pest on many British oyster beds. Some twenty years ago it was found on the coasts of Holland, where it had apparently been transported across the North Sea attached to floating wreckage or possibly seaweed. Within ten years it had become a serious pest there also, and had also spread north to the coasts of Germany and Denmark. During the hard years of the recent war the Dutch were driven to utilize this previously unwelcome visitor as a source of human food.

There remain to be mentioned the effects of major engineering works on marine life. The author was first struck by these during a visit to the Carnegie Marine Biological Laboratory on the Tortugas Islands in the Gulf of Mexico. On one of the sandy coral cays arises the immense brick erection of Fort Jefferson, now derelict (figure 3). This is surrounded by a moat which was originally in free communication with the sea and in which became established a representative sample of corals and other marine organisms. In 1919, hurricane seas breached the moat, sand and debris were carried in, and free circulation ceased: it became a sediment trap. In 1934 the fauna of the moat was very different from that when the sea had free access. Only those organisms which could withstand silty conditions survived, and these included only one out of originally seven species of corals, namely *Siderastrea radians*. But the most noteworthy fact was that many of these colonies had become more rounded and had

changed in skeletal form; in this way they had become capable of living in water where there was a continuous fall of sediment.

One of the greatest feats of marine engineering was the cutting of the Suez Canal (figure 7). In 1924, fifty-five years after the canal was opened, the fauna was studied by a Cambridge University expedition under Professor H. Munro Fox. The greatest barrier to the migration of animals through the canal is the high salinity of the Bitter Lakes, originally a dry valley but with salty deposits resulting from the drying up of a former northward extension of the waters of the Gulf of Suez. To a less extent the narrowness of the canal proper, and the stirring up of water in it by the passage of boats, affect large and small animals respectively. But despite these factors and the high temperature of the shallow water, there is now a representative marine fauna in the waters of the canal and its lakes. The animals are predominantly Red Sea species, because powerful currents flow from the Red Sea into the Bitter Lakes, while there is a slow current from there into the Mediterranean for ten months of the year. Only in fish are Mediterranean species well represented, because these move independently of currents. The invertebrate animals are distributed mainly during the drifting planktonic stage of the life-history and so are at the mercy of prevailing currents. Gradually, representatives of the Indian Ocean fauna are passing through into the Mediterranean, where two of them, a pearl oyster and a swimming crab, are now firmly established.

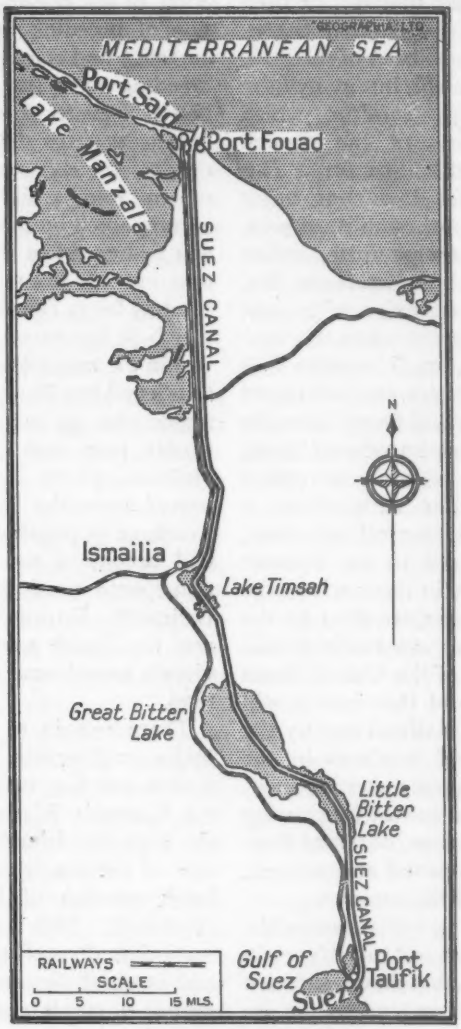


FIGURE 7 – *The Suez Canal.*

The Dutch, in the latest and greatest of their battles with the sea, completed a great dyke (figure 5) across the mouth of the Zuider Zee in June 1932. By so doing they converted a wide area of saline water into a great inland lake. Before the dyke was finished a thorough survey of the animals and plants within the Zuider Zee was made, and subsequent changes in both the environment and the population were closely followed. Originally the latter consisted of a somewhat restricted though essentially marine community, but included a number of endemic species of both plants and animals. Decrease in salinity was accompanied by rise in nutrient salts and so in basic fertility, and there was a widespread change in the fauna and flora. Purely marine species, such as herring, anchovies, plaice, mussels, cockles, and crabs, and also a seal colony on the island of Urk, all disappeared. Porpoises were asphyxiated under the ice which formed on the now fresh water. Brackish-water or estuarine species, notably the solitary endemic crab, maintained themselves to some extent, but fresh water forms which migrated down from the rivers became dominant within two years after the completion of the dyke. These included bass and carp among fish, many fresh-water plants, and also invertebrates such as the harlequin fly, *Chironomus*, which breeds in water. This became so numerous in the initial absence of enemies, that the hordes of flies arising from the water blocked the radiators of cars driving over the dyke.

After the repair of damage suffered during the war, the eventual outcome of this major change brought about by the activities of man will be the conversion of a shallow arm of the sea into a restricted and reed-bordered lake. This will be rich in fresh-water life but will probably contain a few curious remains as sole evidence of its original saline character.

Sydney Young, 1857–1937

J. TIMMERMANS

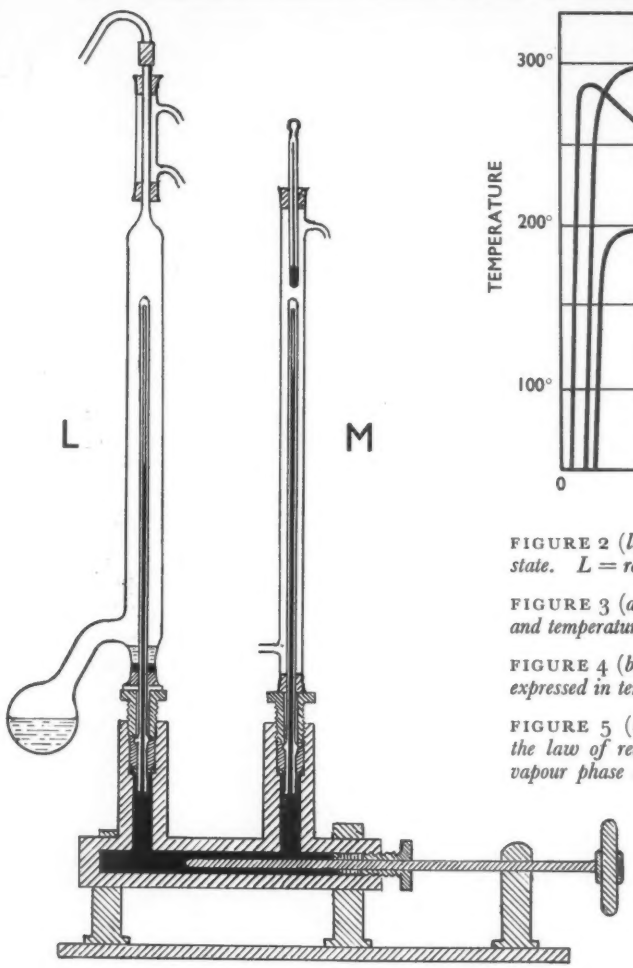
The preparation of organic compounds of a very high degree of purity is of great practical and theoretical importance. To the experimentalist Sydney Young we owe both recognition of the significance of such substances and the development of elegant new practical methods of obtaining them. Young's eminently reliable work influenced that of scientists in many countries and especially in Belgium, where there was already a well-established tradition in the preparation of pure organic compounds for stoichiometric and other studies.

Gas chemistry has always held a place of honour in Great Britain, where much fundamental research on gases has been done. The names of Boyle, Hales, Priestley, Dalton, Cavendish, Davy, Faraday, Andrews, Dewar, and Ramsay immediately spring to one's mind in connection with research in this field. These scientists will always be remembered for the originality of their work. After the early explorers who daringly advance into the unknown come the settlers who take possession of the land and occupy it permanently. In the realm of science this second generation is represented by the experimental scientists whose aim is to establish a precise measuring technique. The reputation of these meticulous workers is more slowly established because their work is less spectacular, but with the passing of time the importance of such investigations as an indestructible basis for further progress becomes apparent. Sydney Young is an important representative of this class of scientific worker—critical rather than creative, but eminently reliable.

FIGURE 1 – *Sydney Young.*

Young, a Lancashire man, studied under Roscoe and Schorlemmer at Owens College, Manchester, and under Fittig at Strasbourg. He obtained his degree as Doctor of Science in 1883, while working with Ramsay at University College, London, where he graduated in 1880. In 1887 he succeeded Ramsay as Professor of Chemistry at University College, Bristol, a position which he occupied for the next fifteen years: this was the most fruitful period of his scientific career. In 1903, at the age of 46, he became Professor of Chemistry at Trinity College, Dublin. There the burden of work connected with teaching and examinations left him time for little more than theoretical interpretations of his earlier experiments. He was chairman of the chemistry section at the Annual Meeting of the British Association at Cambridge in 1904, chairman of the Royal Irish Academy, and a Fellow of the Royal Society.

This is not the place for a detailed chronological account of Young's researches or of the papers he published. This may be found in the excellent biographical studies made by his successor at Bristol, Professor Francis Francis (*Journal of the Chemical Society*, 1937, 1332), and by his old pupil in Dublin, Dr W. R. G. Atkins (*Royal Society Obituary Notices*, 1937, **2**, 371). Here it will suffice to give a general outline of the activities of the great experimentalist. There was a remarkable uniformity in his career; he devoted some twenty years of his life to a study of the thermodynamic properties of, and the heterogeneous equilibria between, about thirty highly purified organic compounds. The results of these researches appeared in 1908 in his book *Stoichiometry*. In preparing the pure substances required for his researches he improved the existing methods and apparatus used for fractional distillation. His observations



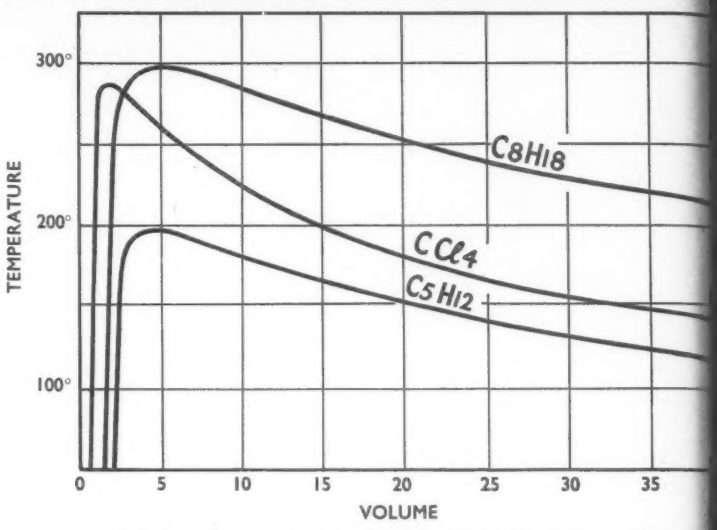
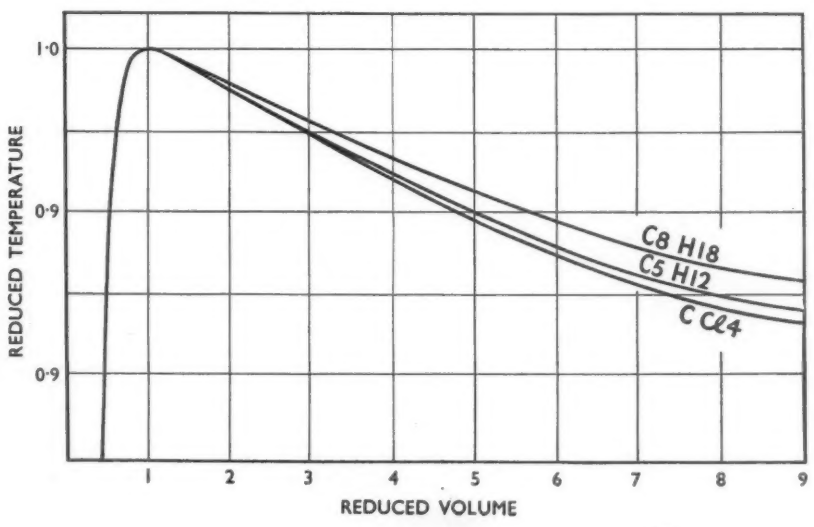


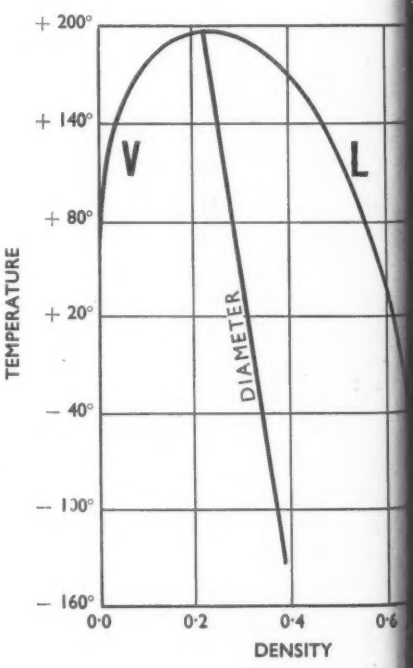
FIGURE 2 (*left*) – *Ramsay-Young apparatus for studying the equation of state. L = reaction tube. M = gas manometer.*

FIGURE 3 (*above*) – *Specific volumes of liquid and saturated vapour in c.c. and temperature in degrees Centigrade (orthobaric volumes).*

FIGURE 4 (*below, left*) – *Reduced orthobaric volumes of the same substances expressed in terms of critical volume and critical temperature.*

FIGURE 5 (*below, right*) – *Orthobaric density of n-pentane, illustrating the law of rectilinear diameters (see page 13). V represents the saturated vapour phase and L the liquid.*





in this field were embodied in a second treatise, *Distillation, Principles and Processes*, of which the first edition was published in 1922.

Young's first experiments on heterogeneous equilibria were suggested to him by Roscoe and carried out under the supervision of Ramsay. Their object was to examine the behaviour of saturated vapour, crystal, and liquid phases in the neighbourhood of the triple point. Shortly afterwards, however, he specialized in precise determinations of the thermal constants, density, vapour pressure, and critical constants of a great number of organic substances, such as acetic acid, benzene and its halogenated derivatives, cyclohexane, paraffins, carbon tetrachloride, alcohols, and esters of the fatty acids. These researches established for Young a reputation for impeccable precision. As his means were limited he built his own glass apparatus—these are models of ingenuity and simplicity (figure 2). In making determinations of temperature, specific volume, and saturated vapour pressure he not only took the greatest care in making all the corrections needed for the high accuracy he achieved, but managed to avoid making his technique unnecessarily complicated. His mastery of technique is illustrated by his use of ordinary thermometers, graduated in degrees on the stem, for his extremely precise measurements of temperature. These thermometers were, however, prepared with great care. To avoid variations in the zero point they were annealed in a bath of boiling naphthalene. He himself made the table of corrections for all parts of the scale by suspending the thermometer in vapour from pure boiling liquids, a method still regarded as giving reliable standards. The accuracy of his results is such that even after fifty years they remain unquestioned.

Young's magnificent work in the determination of constants is important not only because it gives so many precise data relating to fundamental experiments, but because it is of significance in assessing the validity of the equation of van der Waals. Young was able to demonstrate that, generally speaking, his quantitative results conformed well with theory at every point, but that certain numerical coefficients had to be altered. For example, the critical coefficient $D_{cr.}/D_{calc.}$, where $D_{calc.}$ is the density (specific volume) obtained by applying the laws of perfect gases at the critical temperature and pressure, was assigned the value 2·7 by van der Waals, whereas observation gives the value 3·8. The theory of corresponding states is more accurate than the equation of van der Waals from which it is derived (see figures 3 and 4). Young also tested very carefully the so-called law of rectilinear diameters, which states that if the mean of the densities of the liquid and saturated vapour at any temperature be plotted against the temperature, the points so obtained will lie on a straight line. In only one case, that of normal pentane, was the law exactly followed; the curves for all the other liquids examined showed a slight but distinct curvature. (See figure 5.)

The care taken by Young in the execution of his very precise measurements places him on the level of physicists like Regnault. His pioneering work lay in the preparation of organic compounds in a state of high purity, for his exact determinations of the critical constants of a large number of substances showed him how sensitive these constants are to traces of impurities. Before his time only Mendelejeff, using ethyl alcohol, and de Visser, using acetic acid, had demonstrated the possibility of preparing completely homogeneous, anhydrous organic substances characterized by the constancy of their physical properties. Young verified this for a large number of substances, and his success was such that, in the great majority of cases, his values are still accepted as standards today. There again he devised methods of overcoming difficulties which were so simple and effective that they are still used.

His experimental work entailed the determination of the boiling-points of a large number of homologous compounds in various organic series. He was able to demonstrate that on the Kelvin scale the difference (Δ) between the boiling-points, at normal pressures, of two successive members of such series depends only upon the boiling-point of the first member. In general the results conform well with the general formula

$$\Delta = 144{\cdot}86/T^{0{\cdot}0148\sqrt{T}}$$

This is one of the few stoichiometric relationships which have real quantitative significance.

His work on the preparation of pure substances compelled Young to devise improvements in the methods of distillation and in the design of dephlegmators then in use. The 'evaporator still-head' and column of Young and Thomas was the first apparatus which made possible the separation of *n*-pentane (boiling-point 34·5° C) from *iso*pentane (boiling-point 29·0° C), both of which are contained in light petroleum.

To Young also we owe both new experimental methods, and new ways of representing the

resulting data, which have proved of great practical importance in the laboratory and in industry. He discovered large numbers of azeotropic mixtures and pointed out simple methods of determining their composition: this opened a new and very fruitful field of science. He determined the exact composition of some ternary azeotropic mixtures, and his process for the dehydration of ethyl alcohol by elimination of the water in the form of a ternary azeotropic mixture with benzene has been employed in the Kahlbaum works in Germany.

While Young was engaged in this important research during the last decade of the nineteenth century, several other British scientists were also engaged in the study of very pure substances. Perkin was interested on account of his work on magnetic rotatory power, and Thorpe because of his measurements of viscosity. Although Young did not establish a school of his own in England, his work has long influenced foreign scientists, particularly in Belgium and in the United States.

Belgian chemists had a well-established tradition of particularly conscientious work in connection with the preparation of pure substances. This work was originated by Jean Servais Stas, who required perfectly pure materials for his determinations of atomic weights, and by Léon Crismer, who demonstrated the importance of the critical temperature of dissolution as a simple and highly sensitive criterion of purity. Crismer used this test to establish the most efficient methods for completely drying methyl alcohol and its homologues. When Belgian chemists became aware of the work of Young there was a swift development of the techniques necessary for the study of pure organic compounds. Chavanne improved the methods used for the identification of mineral oils of different origins, submitting them to fractional distillation and comparing with synthetic samples the fractions so obtained. The work of Chavanne's pupils is marked by the particular care taken in the purification and identification of organic substances. At the University of Louvain, Louis Henry had always attached great importance to stoichiometric relationships in organic chemistry, a study which involves the use of pure reagents. In this connection, Pierre Bruylants and his school have done brilliant research on density and refractive index in the paraffin series. At Ghent, the work of Frédéric Swarts, to whom we owe the characterization of most known organic compounds of fluorine, is marked by the care taken in the purification of samples used for some of the determinations, notably for measurements of refractive index and heat of combustion.

This combination of favourable circumstances led to the creation in Brussels, in 1921, under the auspices of the Union Internationale de Chimie, of the Bureau of Physico-chemical Standards, where the main physical constants of nearly two hundred of the commonest organic compounds have been accurately determined. It was in Brussels too that Lecat started his chemical researches, now so extensive and fruitful, in the field of azeotropism.

In the United States, departments of the Bureau of Standards in Washington have undertaken, under the guidance of Professor Washburn, some important work on the identification of very pure petroleum hydrocarbons, and on their heats of combustion. Other researches, notably those carried out in California, relating to the measurement of changes in entropy, have necessarily led to the preparation of great numbers of pure organic compounds. In the United States the influence of Young is also felt, though indirectly, through two former students of the University of Brussels. Albert Henne, professor at Columbus University, Ohio, has done fine work on organic compounds of fluorine which combines characteristics of the schools of both Chavanne and Swarts. Georges Callingaert, director of the research department of the Ethyl Gasoline Corporation, Detroit, has successfully undertaken the study of very pure hydrocarbons.

It is thus evident that the example set by Young has started several important schools of research on pure organic compounds. Scientific workers had too long been content to deduce so-called constants from measurements carried out on only approximately purified samples, and there was a manifest discrepancy between the accepted standards of chemical purity and the standards of accurate physical measurement. In the inorganic field it had long been recognized that each definite compound is characterized by physical constants which, provided the process of purification has been properly carried out, are independent of the origin of the sample. The instability of organic substances, together with the difficulty of purifying them and of keeping them pure, led to the belief that this was not so in organic chemistry. It is to Young that we owe the convincing demonstration that a pure organic substance is as precisely defined as one of the elements themselves, and on this rests his main title to fame.

Some applications of optical crystallography

N. H. HARTSHORNE

During the last fifteen or twenty years, the polarizing microscope has proved its worth in the identification and analysis of solid substances, not only in pure science but in industry and technology. By its use, for example, members of a series of closely related compounds may easily be distinguished from one another, the individuals in solid mixtures of salts can be identified, organic stereoisomers may be differentiated, and the nature of the solid phases in such forbidding systems as high-temperature silicate mixtures can be ascertained.

The determination of the optical properties of transparent crystalline substances by means of the polarizing microscope forms, as is well known, the basis of a standard petrological technique for differentiating and identifying the mineral species in rocks. It is perhaps not so well known that this method of identification has also found many useful applications in other fields, notably in general chemical practice and in the study of a variety of natural and industrial products, including refractories, slags, building cements, explosives, plastics, and textile fibres. Several authors [1] have drawn attention to the wide applicability of the method, which is illustrated in the present article. For greater clarity it has been thought desirable also to include an outline of the underlying principles of the method.

Two other crystallographic methods of identification are based respectively on the measurement of characteristic interfacial angles, and the use of X-ray powder spectrograms as 'fingerprints.' The first of these can be applied only to well-formed crystals of individual compounds which are large enough to be mounted on a goniometer. The second method can be directly applied to mixtures, and is particularly useful when the state of division of the material is near, or less than, the limit of microscopic resolution. But where this is not so, it will commonly be found that the optical method is quicker, simpler, and more appropriate. Moreover this method has the advantage that it gives direct information about the texture of the specimen, the form and size of its particles, and, if it is a mixture, the distribution of its ingredients, all of which may be of prime importance in the problem on hand.

The essential features of crystal optics are as follows. Crystals of the cubic system are *isotropic* to light, that is, light passes through them with the same velocity in all directions. Crystals of all other systems are *anisotropic*: their structure and therefore their physical properties, including the velocity of propagation of light, are different in different directions. When a beam of light enters such a crystal, it is in general refracted into two beams which have different velocities and are polarized in planes at right angles to one another. There are, however, certain directions called *optic axes* along which this double refraction does not occur. Tetragonal, hexagonal, and trigonal crystals have one such direction and are therefore termed *uniaxial*; orthorhombic, monoclinic, and triclinic crystals have two, and are termed *biaxial*.

It follows that every section of an anisotropic crystal (except sections normal to an optic axis) has two directions of vibration, corresponding to different refractive indices, along which light entering at normal incidence is constrained to vibrate. In most cases these vibration directions are the same, or nearly the same, for all wavelengths; the refractive indices associated with them vary, of course, with the wavelength.

The maximum and minimum refractive indices of a crystal for a particular wavelength, together with, in the case of biaxial crystals, the index for light travelling along an optic axis, are known as *principal refractive indices*, and are important optical constants characteristic of the substance. In uniaxial crystals, one of these (ω) is the same for all directions of propagation, and the other (ε) is the index which differs most widely from it. In biaxial crystals, the maximum and minimum indices are denoted by γ and α respectively, whilst that for light travelling along an optic axis is denoted by β.

The equipment required for most optical crystallographic work is quite simple, and the set shown in figure 2 is adequate for all normal

problems. The essential item, the polarizing microscope, is a compound microscope fitted with a rotating stage and two nicol prisms (or 'Polaroid' plates in some modern British and American models[1]). The lower nicol (*polarizer*) is fitted below the stage, and the upper one (*analyser*) at some position above the objective. When both nicols are in position and 'crossed,' cubic crystals can be distinguished immediately from anisotropic crystals, since the former remain as dark as the rest of the field in all positions, whilst the latter in most positions exhibit *polarization colours* (if white light is used) but 'extinguish' at intervals of 90° as the stage is rotated. The reasons for these phenomena are that isotropic material has no effect on the vibration direction of the light from the polarizer, but anisotropic crystals resolve this light into a 'fast' and a 'slow' beam, components of which interfere in the analyser. Only part of the spectrum emerges in phase, and so the light seen is coloured. As the stage is rotated, the vibration directions of the crystal become parallel to those of the nicols every 90°, and extinction results because at these positions the crystal does not affect the vibration direction of the light from the polarizer (see figure 1). Observations of the effect of compensators (crystal wedges and plates of known optic orientation and birefringence—see figure 2) on the polarization colour shown by a crystal section enable its 'fast' and 'slow' vibration directions to be found.

By illuminating a crystal between crossed nicols with a strongly convergent beam of light and bringing to a focus rays which have passed through the crystal in parallel directions, an *interference figure* is obtained. This consists in general of a pattern of polarization colours and bands of darkness. A study of the characteristic patterns given by certain sections of the crystal reveals whether it is uniaxial or biaxial, and in the latter case enables the angle between the optic axes to be measured. It is also an important means of determining the orientation of the principal vibration directions (that is, those associated with the principal indices) with respect to the external form of the crystal.

Refractive indices are determined with the polarizing microscope by making use of the fact that when a crystal is immersed in a liquid having the same index, the crystal/liquid boundary disappears. It is therefore only necessary to mount portions of the material in a succession of liquids of known index until one is found in which the crystal border is invisible. The search is facilitated by the fact that the greater the difference between the indices of crystal and liquid, the stronger is the relief in which the former appears, and also by observations of the so-called Becke line. The latter is a bright line of light which appears, under suitable conditions of illumination, just inside the medium of higher index, and (a more certain indication) which moves farther into that medium when the microscope tube is slightly raised. The two indices of a birefringent section may be

[1]Such microscopes are now being produced by Messrs. Cooke, Troughton, and Simms, and by the Spencer Lens Company. The advantages are that a wide aperture may be provided without undue expense, the construction of the microscope is simplified, and the maker is independent of the supply of Iceland spar of optical quality, which is not abundant.

FIGURE 1 – *Isolation of the beams transmitted by a crystal section. In both positions shown the crystal would be 'in extinction' between crossed nicols. The long horizontal arrows represent the vibration direction of the light from the polarizer.*

(a) Vibration direction AB of crystal parallel to vibration direction of light from polarizer; no light vibrating parallel to CD is transmitted.

(b) Crystal turned through 90°. Vibration direction CD of crystal now parallel to vibration direction of light from polarizer; no light vibrating parallel to AB is transmitted.

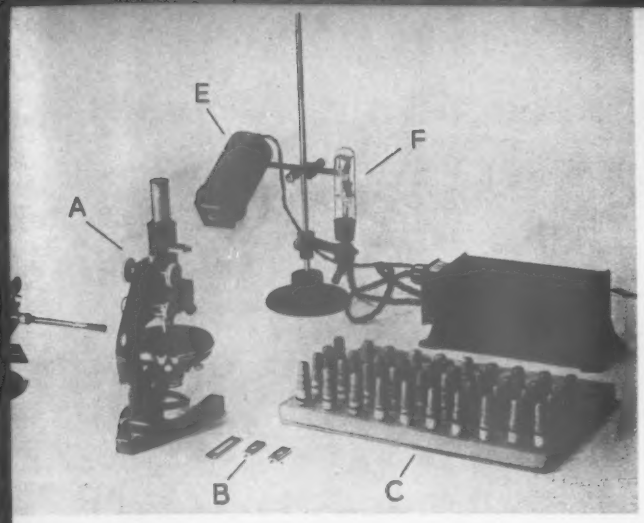
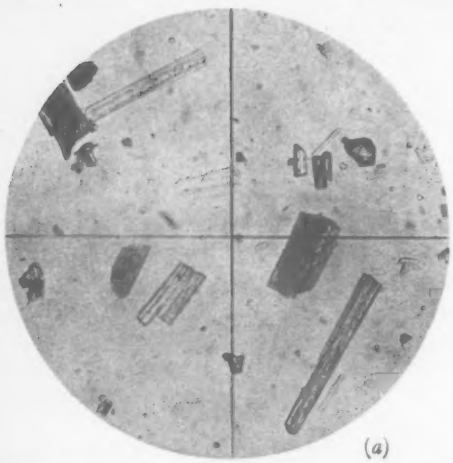


FIGURE 2 (*left*) – *Equipment required for determining optical crystallographic properties.*
A = *Polarizing microscope.*
B = *Compensators (quartz wedge, ¼-wave mica plate, 1-wave gypsum plate).*
C = *Mounting liquids of known refractive index.*
D = *Abbé refractometer for checking values of C.*
E = *Source of white light.*
F = *Sodium lamp.*


(*a*)

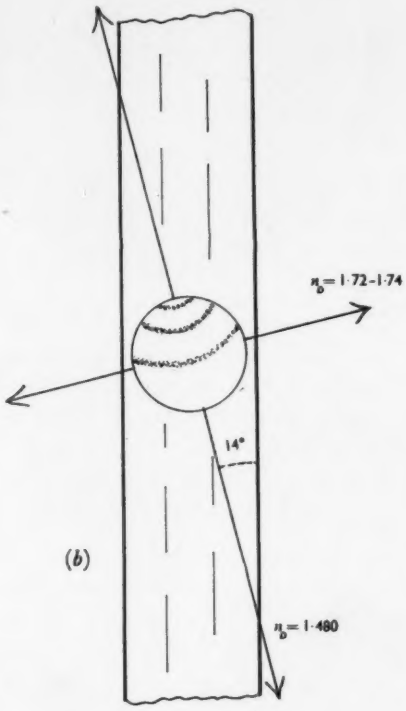
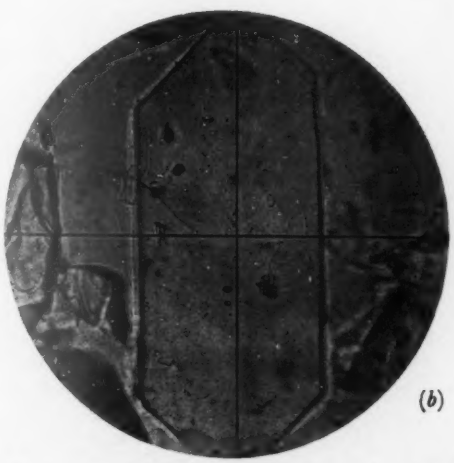
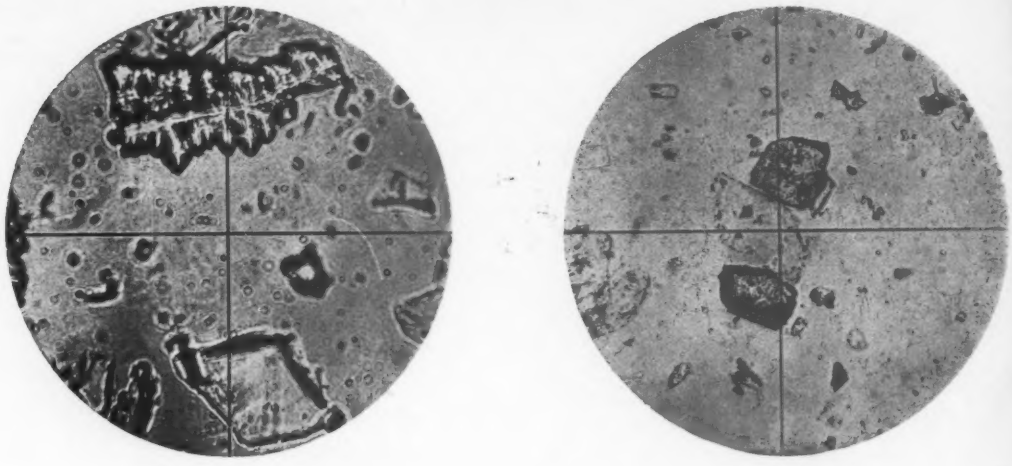


FIGURE 3 – *p-Nitrobromobenzene.*
ounted in liquid of index 1·494 (*D*) (× 100) *in polarized light g parallel to horizontal cross-hair. Crystals lying nearly parallel to ection show weak relief, since the index for light vibrating along their is near that of the liquid. (See* (*b*).)
tical properties of section presented by crystals in (*a*).

(*a*)


(*b*)

GURE 4 – *Crystal of* $NH_4H_2PO_4$ *mounted in liquid of index* 1·531 (*D*) *in polarized light* (× 100). *Substage aphragm nearly closed.*
) *Light vibrating vertically, parallel to the* ε (1·479, *D*) *vibration direction. Note strong relief.*
) *Light vibrating horizontally, parallel to the* ω (1·525, *D*) *vibration direction. Crystal and liquid are nearly matched.*
both cases note Becke line just outside border of crystal, indicating $n_{liquid} > n_{crystal}$.

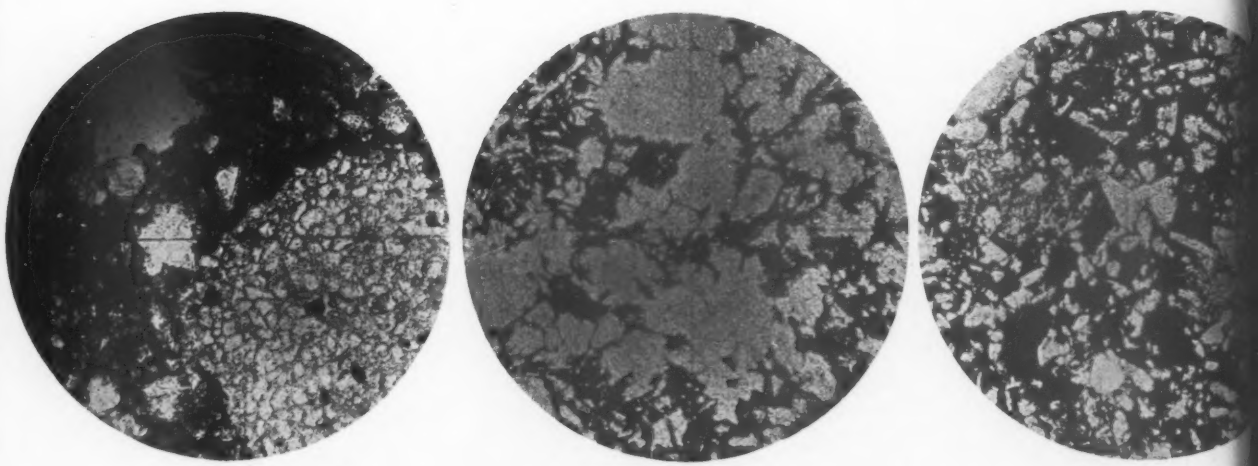


(*a*) (*b*)

FIGURE 5 – *Distinction between salt mixtures having the same ions.*

(*a*) $PbCl_2 + Ba(NO_3)_2$ *in liquid of index* 1·633 (× 480). *Substage diaphragm nearly closed. Dendritic crystal of* $PbCl_2$ (*birefringent,* $n_D = 2{\cdot}199$–$2{\cdot}260$) *in upper half of figure shows Becke lines inside crystal border. Large crystal of* $Ba(NO_3)_2$ (*isotropic,* $n_D = 1{\cdot}571$) *in lower half of figure shows Becke line outside crystal border.*

(*b*) $Pb(NO_3)_2 + BaCl_2.2H_2O$ *in same liquid* (× 100). *In centre of figure are two large crystals of* $Pb(NO_3)_2$ (*isotropic,* $n_D = 1{\cdot}7815$) *in strong relief, with crystal of* $BaCl_2.2H_2O$ (*birefringent,* $n_D = 1{\cdot}635$–$1{\cdot}660$) *between. The latter shows in weak relief, since* $n_{liquid} \approx n_{crystal}$.



(*a*) (*b*) (*c*)

FIGURE 6 – *Thin sections of silica brick* (× 50).

(*a*) *Soft-burned brick before use. Light area (lower right) is ganister fragment consisting of unaltered quartz. Remainder largely interstitial material consisting of unaltered quartz grains, with cristobalite and glass.*

(*b*) *After use as roof brick in open-hearth furnace. Inner zone, consisting of isotropic cristobalite (white grains in figure) and magnetite (dark ingredient) from furnace charge.*

(*c*) *Ditto, tridymite zone. Tridymite (white in figure) in typical prisms and 'arrowhead' twins, one of which is seen just above the centre of the figure.*

eparately compared in this way with that of the iquid by using polarized light and isolating the wo beams as explained in figure 1.

Figure 4 illustrates the application of this nethod to ammonium dihydrogen phosphate, a niaxial substance which habitually crystallizes in quare prisms with pyramidal ends. These crystals ie on their sides, and in this position they present oth of the principal indices, ε being that for light ibrating along the length of the prism, and ω hat for the transverse direction.

In such cases the determination of the principal ndices is a simple matter. It frequently happens, owever, especially with crystals of low symmetry, hat the most prominent faces, which determine ow the crystals lie on the slide, are parallel to one of the principal vibration directions, and so he indices shown have intermediate values. imple methods are available for determining the rincipal indices of such crystals, and also of rystal grains and fragments possessing no characeristic external form which adopt random positions on the slide, but space does not permit of heir being described here. It should be said, owever, that it is not always necessary to deterine the principal indices of a substance in order o identify it. Figure 3 illustrates a case in point. -Nitrobromobenzene habitually crystallizes as hown in (*a*), and nearly all the crystals lie so as o present the optical characters shown in (*b*), hich gives the inclination of the vibration direcions to the long axis of the crystal, the refractive ndices (neither of them a principal one), and, in he central circle, the interference figure. Proided that the substance does not adopt some adically different habit, this combination of ptical properties can be used to identify it.

The following examples are only a few of he very many that could be quoted to illustrate he value of the optical method, but they serve o show something of the range of problems overed.

The qualitative chemical analysis of a mixture f salts reveals merely what ions are present. For xample, suppose that barium, lead, nitrate, and hloride ions are found. Does the mixture consist f $PbCl_2$ and $Ba(NO_3)_2$, or of $Pb(NO_3)_2$ and $BaCl_2.2H_2O$, or of some other possible variaion? A knowledge of their refractive indices nd of the fact that the two nitrates are isotropic nables a decision to be reached in a matter of inutes, merely by mounting the mixture in a iquid having an index intermediate between the xtreme values shown by the salts and observing the Becke line and the behaviour between crossed nicols (see figure 5).

Some years ago, the author had occasion to examine some specimens of potassium mercuric iodide and ammonium dihydrogen phosphate, the purity of which was in doubt [2]. Under the microscope the former was seen to contain colourless isotropic crystals with a refractive index slightly greater than 1·66. This showed that the impurity was potassium iodide, which is cubic and has an index of 1·67. Associated with the uniaxial phosphate were found fragments which did not show the ω value of this salt, and gave biaxial interference figures. This suggested that the impurity might be the biaxial diammonium salt, and this was confirmed by a determination of the β index. In neither of these cases could the impurity have been identified by chemical analysis.

Numerous examples of the use of the polarizing microscope in organic chemistry have been quoted by Benedict [3]. For instance, in studying the preparation of certain amino acids he was able to save much time by using optical methods of identification (based on data previously obtained by Keenan; see below), particularly in view of the fact that the acids had indefinite melting-points and could not be characterized by this property. A drop of the reaction mixture could be quickly examined with the microscope to see whether in fact it contained the required product, and so no time was wasted in working up the products of unsuccessful runs. Side reactions were also investigated by the same means.

Bennett and his co-workers have used the method as a means of differentiating between organic stereoisomers, a particularly interesting example being the isomeric trithioacetaldehydes [4]. Two isomers only are required by stereoisomeric theory, and an alleged third isomer was found under the polarizing microscope to be a eutectic mixture of these two.

With the objects of demonstrating the value of the optical method in organic chemistry and of adding to the body of published data, a large number of optical crystallographic studies of series of related compounds have been undertaken during the past thirty years, mainly in America. Among the most prolific workers in this field are G. L. Keenan and W. M. D. Bryant. Keenan's studies have included sugars, amino acids, and substances listed in the U. S. Pharmacopoeia [5], while Bryant has studied derivatives of alcohols, aldehydes, and aliphatic acids [6], among many other compounds. It has been found with very

few exceptions that compounds in the same series can readily be distinguished from one another by determining their refractive indices or by other simple optical tests.

The optical method has played a valuable, and in some cases essential, part as a means of identifying the solid phases in phase-equilibrium studies. Thus, in investigations of high-temperature silicate systems, such as have been in progress for some years in America and at the Building Research Station in Britain, ordinary methods of thermal analysis are of little use, since equilibrium is attained so sluggishly. The method mainly adopted is to quench equilibrium mixtures of the components and examine the resulting solid under the polarizing microscope. Any liquid present in the original equilibrium mixture quenches to a glass, which can be recognized by its isotropic character. Crystalline solid phases are identified by their characteristic optical properties. In this way the thermal diagram may be built up. A knowledge of the equilibria in systems of this type is of fundamental importance in petrological research and in the study of cement, slags, and refractories. The classical example, which sheds much light on the constitution of Portland cement, is the system CaO–Al_2O_3–SiO_2 studied by Rankin and Wright [7], and in the same connection the important quaternary system CaO–$2CaO$, SiO_2–$5CaO$, $3Al_2O_3$–$4CaO$, Al_2O_3, Fe_2O_3 has been studied by Lea and Parker [8].

Optical methods play an important part in the study of refractories as such, and a good example is afforded by the changes undergone by silica bricks in the open-hearth furnace. In a soft-burned brick before use the silica is present mainly as quartz (figure 6(*a*)), distinguishable from the other polymorphic modifications of silica by its marked double refraction. During use the silica in the inner and hottest zone of the brick becomes converted to cristobalite (figure 6(*b*)), which is isotropic and thus immediately identifiable between crossed nicols. Adjoining this zone is a somewhat cooler one, where the silica has been converted to tridymite (figure 6(*c*)), which has a low double refraction, and also crystallizes in characteristic shapes. The widths of these zones show the temperature gradient to which the brick has been subjected, and this is an important factor in the life of the furnace lining.

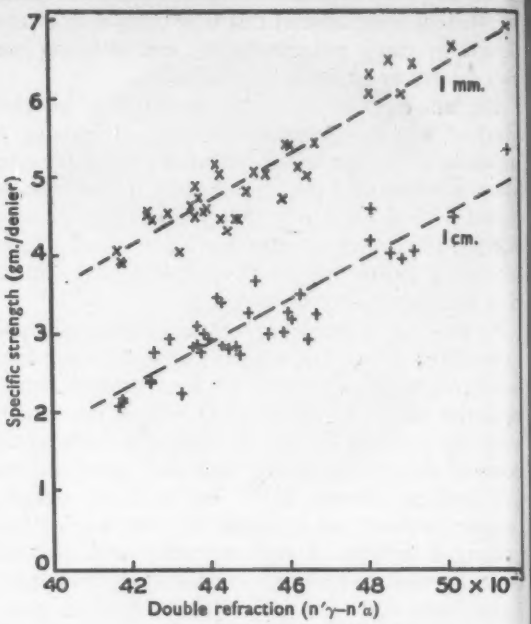


FIGURE 7 – *Relation between double refraction and strength of cotton fibres* (1 *mm. and* 1 *cm. lengths*).
(*n'γ and n'α are the indices for light vibrating respectively along and across the fibre.*)
(*Reproduced by permission of the British Cotton Industries Research Association.*)

Numerous investigations on the relation between the optical properties, and in particular the refractive indices, of fibres and their other physical properties have been undertaken. Thus it has been found by the British Cotton Industry Research Association [9] that there is a high degree of correlation between the birefringence of cotton fibres and their strength (see figure 7).

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The principles of chromatography

A. J. P. MARTIN

Chromatography is a method of chemical analysis founded on differential adsorption in a counter-current process. Although the basic procedure of the method was very firmly established by the Polish botanist Tswett more than thirty years ago, it is only during the past decade that chemists have recognized its great value and made effective use of it. Dr Martin here describes the principal features of the practical technique, and discusses some theoretical considerations of importance in the use of the method.

Chromatography has been so widely used in the last fifteen years that to give an adequate account of its achievements would be a problem as difficult as to give an account of the achievements of distillation. Since its first use in the form of capillary analysis by Schönbein (1861) and its later development by Tswett (1906), chromatography is already quite indispensable in many fields, and may be expected to become so in any field where the separation of very similar substances is required. Although chromatography has a remarkably wide field of application, the method rests on principles which can be described without reference to specific examples. In the following discussion my illustrations are confined largely to partition chromatography with which I have myself been associated, not because it is more important but because it is less familiar.

Chromatography is a counter-current, or column, process. It bears the same relationship to simple methods of separation by adsorption, in which the adsorbent is merely stirred with the solution, as distillation with a fractionating column does to simple distillation. The analogy with the fractionating column is indeed close. Just as distillation with a fractionating column is equivalent to thousands of separate distillations, so chromatography, with its ordered movement of liquid relative to the adsorbent with which it is continuously equilibrating, is equivalent to a repeated stirring up with adsorbent and filtering. In many cases this differential rate of movement permits the separation, with only infinitesimal contamination, of substances whose adsorption is so similar that no useful separation could be obtained by simply stirring with the adsorbent.

The ideal chromatogram consists of a tube containing a column of porous adsorbent through which the solution is percolating. The proportion of liquid to solid at all points is constant, and the flow of liquid is uniform. Suppose now that a solution of some suitable solute runs into the column in place of the pure solvent. If in any thin cross-section of the column the fraction of the solute in the solvent is α, then $(1-\alpha)$ is adsorbed on the solid. Equilibrium between solid and liquid is, in this ideal case, instantaneous, and no diffusion occurs. It is obvious, since a fraction α is moving with the speed of the liquid and a fraction $(1-\alpha)$ is stationary, that the net rate of movement of the solute is α times the rate of movement of the liquid. *This ratio of the rate of movement of the solute to the rate of movement of the solvent* is called the R_F value. This ideal case is shown in figure 1; it has been interpreted by Wilson [1].

In fact, of course, equilibrium is not attained instantaneously. The solute has to move from liquid to solid and *vice versa*, and this has important practical consequences. For rapid equilibrium the distance over which diffusion must carry the solute must be made as small as possible. It is therefore nearly always a mistake not to use a finely ground adsorbent. Figure 2 shows how the band of solute loses its sharp edges when attainment of equilibrium is not instantaneous. The band approximates more and more closely to the 'error curve' shape as it progresses down the column [2].

So far it has been assumed that the ratio of the concentration of solute in the liquid and in the adsorbent at equilibrium is a constant, i.e. a linear adsorption isotherm has been assumed. This is usually not the case. Generally the proportion of solute in the liquid phase rises as the concentration is increased (Freundlich or Langmuir adsorption isotherm). Figures 3 and 4 show the resulting shapes of the bands. The R_F value rises with the concentration; consequently the front of the band moves faster than the back, and the band broadens. The front stays relatively sharp (figure 4), since the layer of diminishing

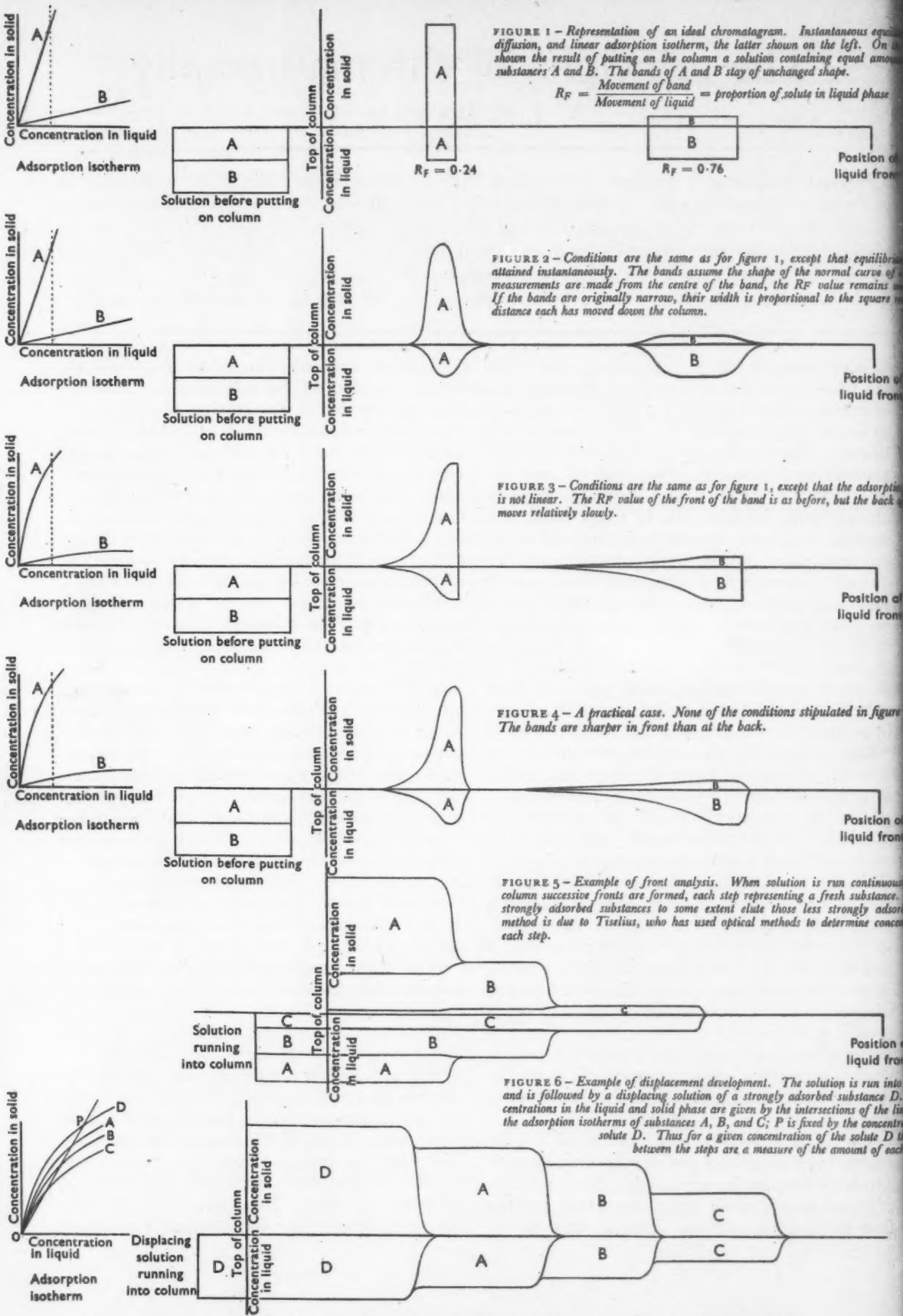


FIGURE 1 – *Representation of an ideal chromatogram. Instantaneous equi… diffusion, and linear adsorption isotherm, the latter shown on the left. On t… shown the result of putting on the column a solution containing equal amou… substances A and B. The bands of A and B stay of unchanged shape.*

$$R_F = \frac{\text{Movement of band}}{\text{Movement of liquid}} = \text{proportion of solute in liquid phase}$$

FIGURE 2 – *Conditions are the same as for figure 1, except that equilibri… attained instantaneously. The bands assume the shape of the normal curve of … measurements are made from the centre of the band, the R_F value remains … If the bands are originally narrow, their width is proportional to the square r… distance each has moved down the column.*

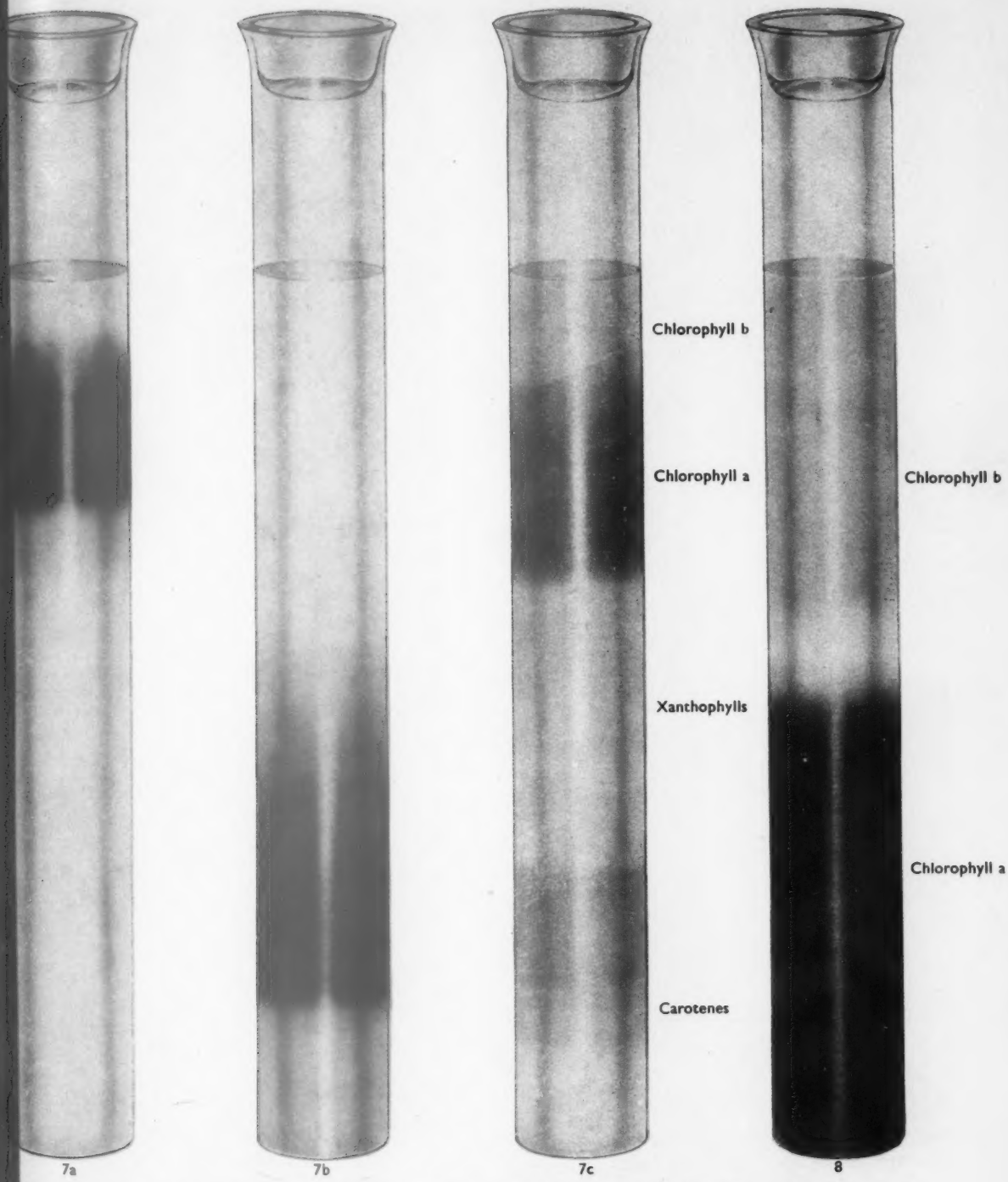
FIGURE 3 – *Conditions are the same as for figure 1, except that the adsorpti… is not linear. The R_F value of the front of the band is as before, but the back … moves relatively slowly.*

FIGURE 4 – *A practical case. None of the conditions stipulated in figure … The bands are sharper in front than at the back.*

FIGURE 5 – *Example of front analysis. When solution is run continuous… column successive fronts are formed, each step representing a fresh substance. … strongly adsorbed substances to some extent elute those less strongly adsor… method is due to Tiselius, who has used optical methods to determine conce… each step.*

FIGURE 6 – *Example of displacement development. The solution is run into … and is followed by a displacing solution of a strongly adsorbed substance D. … centrations in the liquid and solid phase are given by the intersections of the lin… the adsorption isotherms of substances A, B, and C; P is fixed by the concentra… solute D. Thus for a given concentration of the solute D th… between the steps are a measure of the amount of each …*

FIGURES 1–6. *Typical examples of chromatographic adsorption. For further explanation see text.*



GURE 7 – *Stages in the development of the adsorption chromatogram formed when an extract of grass in cyclohexane is sed through a column of starch.*

Start of development. Colourless substances are displacing chlorophyll and carotene. $R_F = 1$, *so no resolution can be seen. Most of the colourless material has been adsorbed, and the carotene band is showing in front of the chlorophyll.* $R_F < 1$. *The coloured bands have been separated, the pigments extracted again into cyclohexane, and the resulting solution passed through a new column. Displacing substances have been left on the old column. Elution development (page 27) shows bands of chlorophylls, xanthophylls, and carotenes.*

GURE 8 – *The same as 7(c), except that for development cyclohexane has been replaced by benzene.*

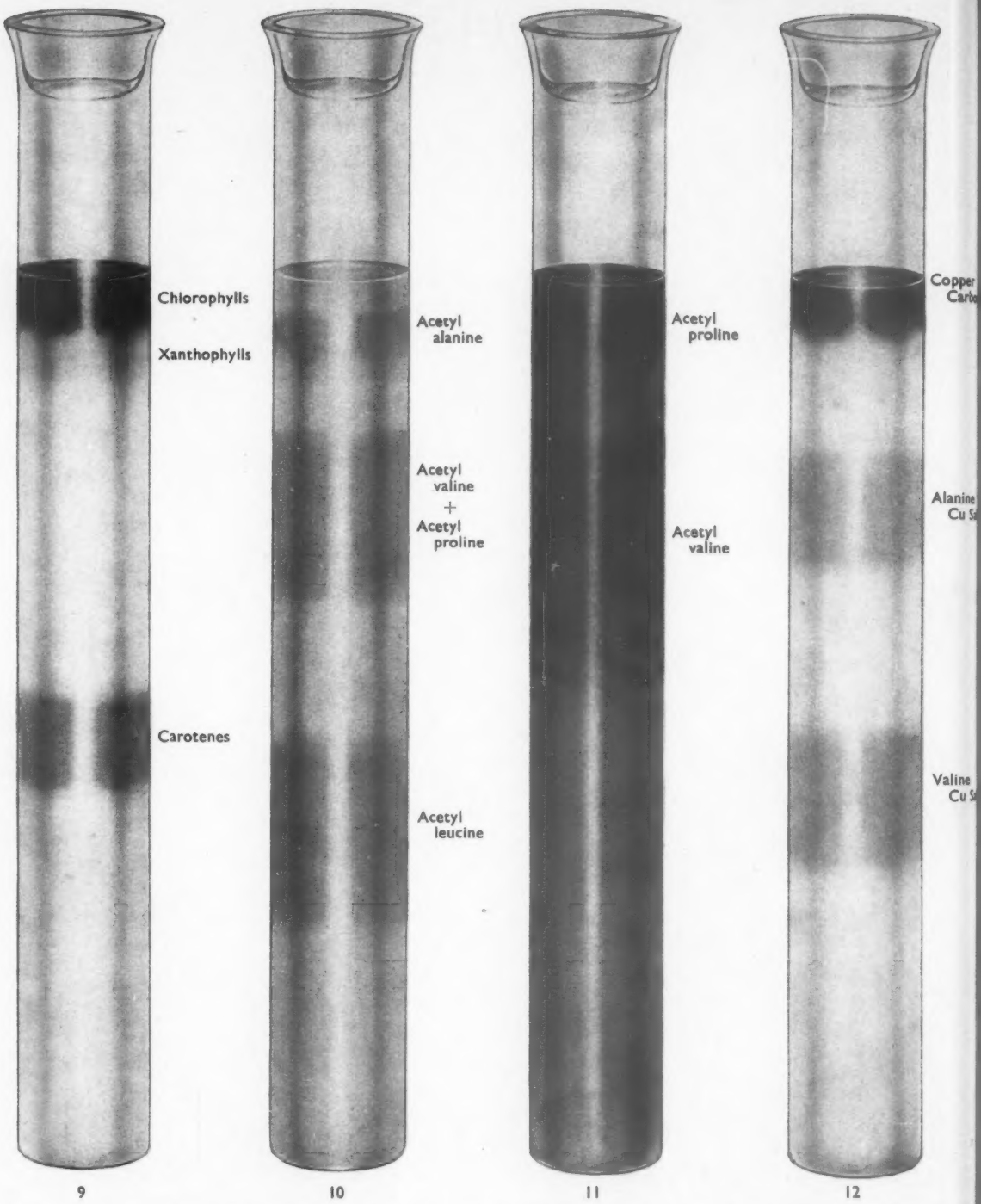


FIGURE 9 – *The same solution as that used for producing the chromatograms shown in figure 7 passed through a column of magnesium oxide. Chlorophylls are strongly retained. Elution development has revealed bands of xanthophylls and carotenes.*

FIGURE 10 – *Partition chromatogram showing separation of acetyl alanine, acetyl valine, acetyl proline, and acetyl leucine on a silica gel column. The silica gel was prepared with water containing methyl orange as indicator, and the position of the acetyl amino acids is shown by the red colour. The solvent is chloroform containing 1% of butanol.*

FIGURE 11 – *Separation of acetyl proline and acetyl valine on a column of silica gel, using a special indicator. The solvent is cyclohexane. Using columns of the type shown in figures 10 and 11, it is possible to estimate quantitatively the amount of alanine, leucine and isoleucine, phenyl alanine, tyrosine, and methionine contained in the hydrolysate of 20 mg. of protein.*

FIGURE 12 – *Separation of the copper salts of alanine and valine on a column of silica gel. The partition chromatogram has been developed with a mixture of chloroform and butanol.*

Partition chromatograms on strips of filter paper. A drop of a solution of amino acids is placed near the top of a strip of filter paper. The strip is hung from a glass trough in an atmosphere saturated with water and solvent. Solvent, also saturated with water, siphons over and down the strip. After 4–48 hours the strip is dried, sprayed with a solution of ninhydrin, and heated. The reagent reveals the position of the amino acids as coloured patches.

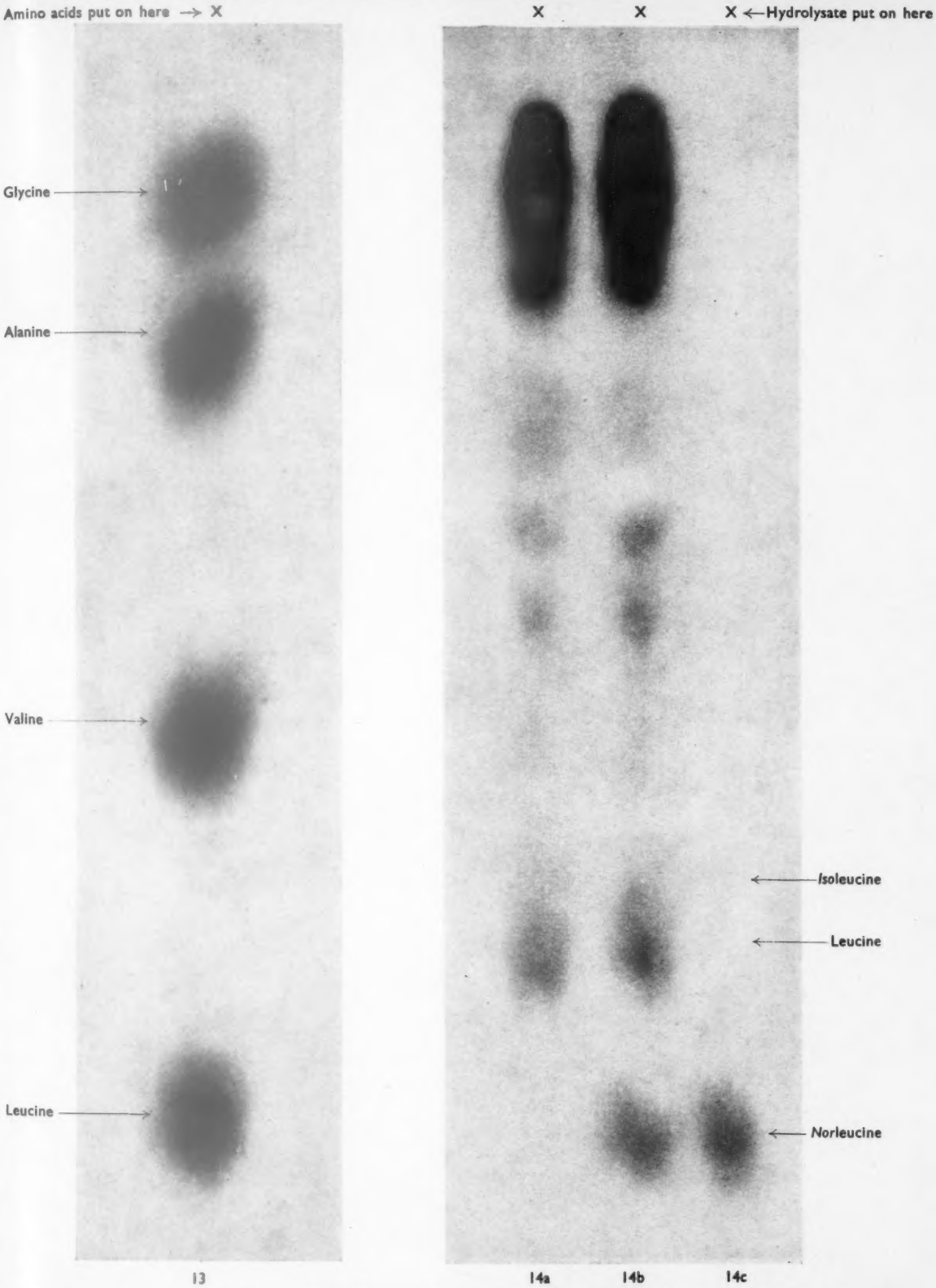


FIGURE 13 – *Separation of glycine, alanine, valine, and leucine, using butanol as solvent.*

FIGURE 14 – *Chromatogram obtained with a hydrolysate of spinal cord, (a) without and (b) with addition of synthetic* norleucine. *In a control experiment (c)* norleucine *alone is used. The solvent is benzyl alcohol. These chromatograms show clearly that, contrary to claims made in the past,* norleucine *is not contained in the spinal cord.*

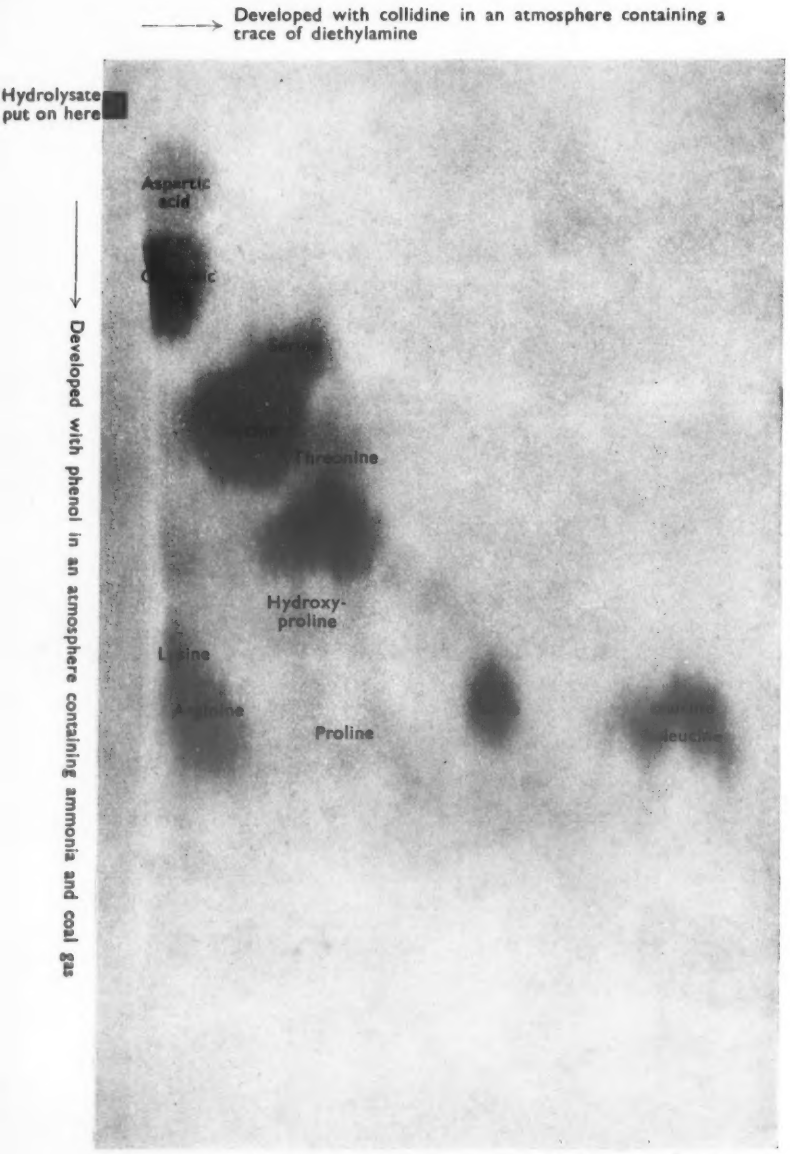

Developed with collidine in an atmosphere containing a trace of diethylamine
Hydrolysate put on here
Developed with phenol in an atmosphere containing ammonia and coal gas
Aspartic acid
Threonine
Hydroxy-proline
Proline

FIGURE 15 – *Two-dimensional chromatogram of gelatin on filter paper. A drop of the hydrolysate is placed near the corner of the sheet of paper. This is hung from the long side and the chromatogram developed with s-collidine.*

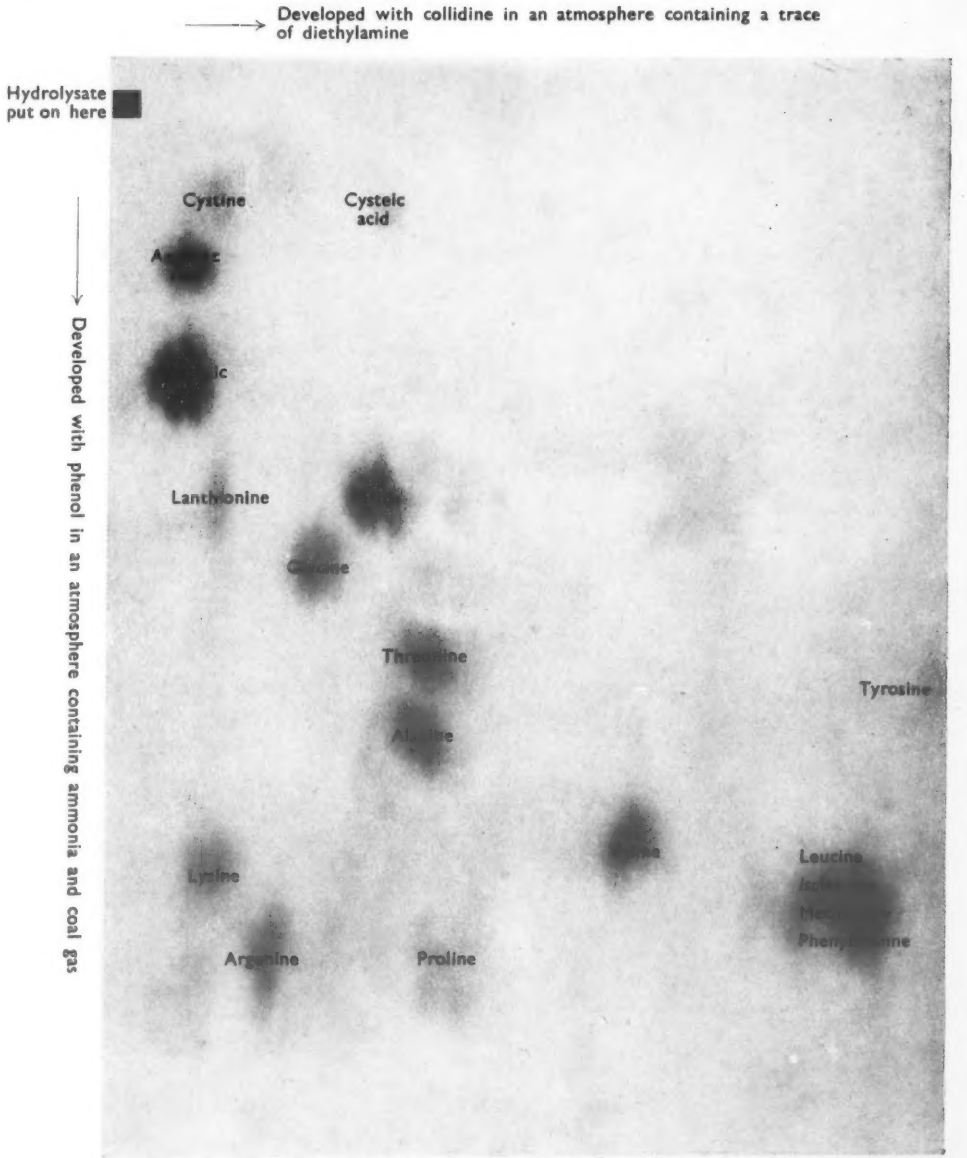


FIGURE 16 – *Two-dimensional chromatogram of tips of wool fibres. Procedure as for figure 15. Exposure to weather and light has converted some cystine to cysteic acid and some to lanthionine. Otherwise the picture resembles that of pure wool. The clump of unresolved amino acids in the*

concentration at the front of the band, caused by diffusion and slow attainment of equilibrium, is continuously overrun by the faster-moving, more concentrated zone behind. The case illustrated in figure 3 has been interpreted by De Vault [3] and Weiss [4].

There is, however, a further complication. The adsorption of one substance may greatly modify the adsorption of another. This is particularly the case when the adsorption isotherms are of the Freundlich or Langmuir type. Figure 5 shows the result of running a relatively large volume of a solution of three substances down a column without 'developing' the chromatogram, i.e. further separating the bands, with pure solvent. If the adsorption of one were not influenced by another, the concentration in the steps would be the same as in the original solution.

If a mixed solution running into the column, as in figure 5, is replaced by a solution of another and more strongly adsorbed substance (*D*), the state shown in figure 6 soon occurs, since each substance 'elutes' or washes off the substance in front of it. In the absence of interaction, elution development would be superposed on a background of *D*. This is interesting as representing a steady state, the bands of *A*, *B*, and *C* moving down the column with unchanging shape.

METHODS OF CHROMATOGRAPHY

Figures 4, 5, and 6 represent three different ways in which chromatograms can be employed. The method of figure 4 (elution development) is the most familiar in the laboratory. After adequate development the column is cut up and the adsorbent extracted with a suitable eluting solvent, or development is continued until the bands run separately from the bottom of the column in the solvent. The latter method of working has been misleadingly named 'liquid chromatography.' In using this method a linear adsorption isotherm is desirable, as otherwise each band tends to tail more or less into the succeeding band.

The method of figure 5, often not recognized as chromatography at all, is extremely widely used in industry for water softening, recovery of valuable ions in industrial wastes, and for solvent recovery from air or other gases. It is remarkable that this solvent recovery process seems to be the only use at present of gas as the mobile fluid in chromatography, though there appears to be no reason why it should not be a valuable method for analytical purposes. Recently Tiselius has applied this method to analysis. He has developed 'front analysis,' as he calls it, into a most powerful tool for dealing with intractable mixtures such as amino acids and peptides. By applying the optical techniques developed for electrophoresis and ultracentrifugal investigations to the liquids issuing from a chromatogram, a peak is obtained wherever the concentration changes. Thus figure 5 would show three peaks.

Tiselius has also developed the 'displacement development' method (figure 6), recording the concentration of the effluent from the column with an automatic interferometer. A record is obtained of a series of steps, the length of each of which is a measure of the amount of each substance present, while the height is determined by the adsorption isotherm.

In distinction to the elution development method, a non-linear adsorption isotherm is an advantage with the last two methods, since the fronts remain sharper and are easier to observe.

ADSORBENTS AND SOLVENTS USED

Alumina and Other Metallic Oxides. The choice of adsorbent and solvent has hitherto been almost entirely empirical. The adsorbent most commonly used in laboratory work is alumina, with non-polar solvents such as petrol. Various metallic oxides and salts behave more or less similarly. The method of preparation of the adsorbent is as important as its chemical composition. Polar and polarizable groups in the solute are the chief determinants of adsorption behaviour with this class of adsorbent. Similarly, elution is caused by polar or polarizable solvents. If a solvent forms hydrogen bonds, it is usually a good eluting agent. These adsorbents differ widely in strength but little in selectivity; the order of bands of different substances is seldom different on different adsorbents of this class.

Carbon. Active carbon, though long used as an adsorbent for decolorizing solutions and for solvent recovery, has only recently been used in analytical chromatography. The adsorption isotherms on carbon are usually far from linear, and it is thus most suitable for 'front analysis' and 'displacement development' (see above). It seems to have several or perhaps many different kinds of adsorbing sites, and carbons with widely different adsorptive selectivity can be produced by different methods of activation. In general it may be said that fatty chains, and particularly aromatic rings, determine adsorption on carbon, while polar groupings are less important. Thus adsorption of amino acids, for example, takes

FIGURE 16 – *Two-dimensional chromatogram of tips of wool fibres. Procedure as for figure 15. Exposure to weather and light has converted some cystine to cysteic acid and some to lanthionine. Otherwise the picture resembles that of pure wool. The clump of unresolved amino acids in the*

FIGURE 15 – *Two-dimensional chromatogram of gelatin on filter paper. A drop of the hydrolysate is placed near the corner of the sheet of paper. This is hung from the long side and the chromatogram developed with s-collidine.*

place from aqueous solution, and they can be eluted by phenol or ephedrine. Pre-treatment of the carbon is usually necessary to prevent irreversible adsorption and catalytic oxidation.

Ion Exchangers. Ion-exchange materials have long been used for water softening but have only recently been used to any great extent in analytical chromatography. They are essentially large insoluble acids or bases which form insoluble salts. The first of such substances to be employed, the zeolites, were unstable in acid solution, and were used to exchange Na^+ for other cations. Adams and Holmes showed that certain synthetic resins possess exchange properties. Sulphonated coal or resins containing sulphonic acid groups are now in use, and will exchange H^+ ions for other ions. There are similarly basic resins which will exchange anions. With these adsorbents the adsorbed molecules are held by electrostatic forces, and it is charge, not molecular structure, that chiefly determines adsorption. Elution is effected by acid, alkaline, or salt solutions.

PARTITION CHROMATOGRAMS

Martin and Synge [2] have introduced silica gel into chromatographic analysis. Dry precipitated silica will take up about half its weight of water without appearing to become wet. A chromatogram can be made with such saturated silica and any solvent not completely miscible with water. With a suitable choice of solvent no adsorption occurs on the silica itself, and the formation of the chromatogram depends entirely upon partition between solvent and water. A typical column is illustrated in figure 10. In such a partition chromatogram the calculated R_F value, derived from the partition coefficient and amounts of water and immiscible solvent, agrees with the observed value.

Other liquids may be used in place of water, and starch, cellulose, or other substances in place of silica. Cellulose in the form of filter paper is a particularly useful material. Using narrow strips of paper it is possible to produce chromatograms analogous to those produced when ordinary columns of material are used. The use of paper strips is illustrated in figures 13 and 14. By using squares of paper (figures 15 and 16) a twofold separation can be effected. The solution to be analysed is applied at one corner of the square and a chromatogram is formed in the same way as when a strip of paper is used. To avoid evaporation the paper must be placed in an enclosure the atmosphere of which is saturated with respect to the solvents used. The paper is then dried, turned through 90 degrees, and the process repeated. A new solvent is used and each 'band' of the initial chromatogram is made the starting-point of another 'strip' chromatogram. The final result is to spread the constituents of the mixture over the whole sheet of paper instead of confining them to the original strip.

The partition chromatogram is highly selective, since solvents may be chosen which associate with particular groupings in the solute. A close analogy can be drawn between the effect of association on the partition coefficient between two liquids and between liquid and vapour. In the latter case association may give rise to azeotropic mixtures.

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[2] Martin and Synge. *Biochem. J.*, 1941, **35**, 1358.
[3] De Vault. *J. Amer. Chem. Soc.*, 1943, **65**, 532.
[4] Weiss. *J. Chem. Soc.*, 1943, 297.

The Chemical Society of London

After a delay of six years occasioned by the war, the Chemical Society (of London) will celebrate the centenary of its foundation on 15th, 16th, and 17th July, 1947. Outstanding among the several important events which will mark the occasion will be the delivery of the Faraday Lecture by Sir Robert Robinson, a past President of the Chemical Society and now President of the Royal Society. The centenary celebrations will be followed by the Eleventh International Congress of Pure and Applied Chemistry, also to be held in London. Many distinguished overseas delegates have been invited to attend, and if all are able to do so there will be seen in London next July perhaps the greatest international gathering of chemists ever to have taken place.

Organosilicon compounds and their industrial development

D. V. N. HARDY

Organosilicon compounds have been investigated for over eighty years, an outstanding contribution having been made by Professor F. S. Kipping, F.R.S., but it was only towards the end of the recent war that mention began to be made of commercial developments. Owing largely to difficulties in obtaining the new materials, first-hand information has hitherto been very scanty, and the precise nature and importance of the substances have been obscured by a secrecy necessitated by both military and commercial considerations.

Although initially studied by a sequence of investigators on the Continent, notably Friedel and his students Crafts and Ladenburg, the chemistry of organosilicon compounds will always be associated with Professor F. S. Kipping and his school of research workers at University College, Nottingham. Starting in 1899, Kipping diligently pursued the subject for close on forty years, and contributed over fifty papers to the *Journal of the Chemical Society*. The work was arduous and beset with experimental difficulty, not the least being a remarkable tendency of the compounds to form amorphous, glue-like products, but with great patience Kipping went on to collect an invaluable mass of precise and detailed information, the accuracy of which has occasionally been challenged but always upheld.

Academic study of organosilicon compounds progressed along classical lines. It consisted chiefly in the preparation and characterization of the various compounds and in the determination of their chemical properties, with theoretical interest focused mainly upon the degree of similarity between organosilicon compounds and their carbon analogues. This similarity proved to be slight. In its ability to combine with itself and with other elements, silicon cannot approach the versatility of carbon, and the facile, subtle variety of organic reactions is not encountered in organosilicon chemistry. Of paramount importance among silicon compounds is the remarkable tendency to form large molecules containing chains, rings, or networks of alternating oxygen and silicon atoms. Silicic acid and the polysilicates are built on this plan, and so are many oxygenated organosilicon compounds.

The methods for preparing organosilicon compounds are few, and consist principally of treating a silicon halide or an alkyl silicate with an organometallic compound or its equivalent. Friedel and Crafts [1] used silicon tetrachloride and zinc alkyls:

$$SiCl_4 + 2Zn(C_2H_5)_2 \longrightarrow Si(C_2H_5)_4 + 2ZnCl_2$$

and Ladenburg [2] showed not only that ethyl orthosilicate may be employed in place of silicon tetrachloride but that arylchlorosilanes can be prepared with mercury diaryls:

$$2SiCl_4 + Hg(C_6H_5)_2 \longrightarrow 2C_6H_5SiCl_3 + HgCl_2$$

Arylsilanes are also accessible by the interaction of silicon tetrachloride, an aryl halide, and sodium [3]:

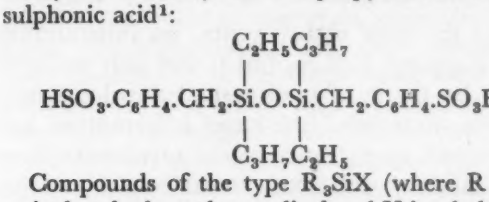
$$4C_6H_5Cl + SiCl_4 + 8\,Na \longrightarrow (C_6H_5)_4Si + 8NaCl$$

A valuable extension was made by Kipping, who introduced the use of Grignard reagents, with all their elegance and flexibility. All these synthetic methods permit the introduction of from one to four univalent organic radicals, either in one operation, by controlling the relative proportions of the reagents, or by successive treatment of the purified intermediate compounds with the same or different reagents:

$$SiCl_4 + CH_3MgBr \longrightarrow CH_3SiCl_3$$
$$CH_3SiCl_3 + C_2H_5MgBr \longrightarrow C_2H_5(CH_3)SiCl_2$$
$$C_2H_5(CH_3)SiCl_2 + C_3H_7MgBr \longrightarrow C_3H_7(C_2H_5)(CH_3)SiCl$$
$$C_3H_7(C_2H_5)(CH_3)SiCl_2 + C_6H_5MgBr \longrightarrow C_3H_7(C_2H_5)Si(CH_3)C_6H_5$$

An immediate consequence is that reaction cannot be confined to a particular intermediate stage, so that not only may yields be poor but the products may be difficult to separate by fractional distillation. Kipping's initial objective was to determine whether silicon resembles carbon in having an equispatial distribution of the four valencies. By the method outlined above he prepared a number

of asymmetric compounds and their salts with optically active bases, but was unable to resolve any compound containing a single silicon atom. He was, however, successful [4] in obtaining the optical antipodes of such compounds as 1, 2-dibenzyl-1, 2-diethyl-1, 2-dipropyldisiloxane-disulphonic acid[1]:



Compounds of the type R_3SiX (where R is a univalent hydrocarbon radical and X is a halogen atom or an alkoxyl group) readily hydrolyse to the corresponding silanols. These are usually high-boiling oils, or even crystalline solids, which may be readily dehydrated to disiloxanes. For example, triethylchlorosilane gives triethylsilanol (b.p. 184° C), which has an odour like camphor, and viscous hexaethyldisiloxane (b.p. 231° C):

$$(C_2H_5)_3SiCl + H_2O \longrightarrow (C_2H_5)_3SiOH$$
$$\longrightarrow (C_2H_5)_3Si.O.Si(C_2H_5)_3$$

Such structures do not admit a greater degree of complexity, but it is quite otherwise with the products obtained by hydrolysing compounds of type R_2SiX_2. By carrying out the hydrolysis under the mildest conditions it is possible to isolate the simple silandiols:

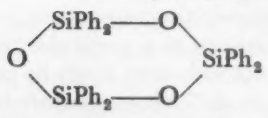
$$(C_2H_5)_2SiCl_2 + 2H_2O \longrightarrow (C_2H_5)_2Si(OH)_2$$

but these are very prone to undergo dehydration, and more complicated products usually arise, such as the syrup of high molecular weight obtained by Kipping and Martin [5] from diethyldichlorosilane. This syrup could be distilled without decomposition below 300° C, and possessed the empirical formula $C_4H_{10}SiO$. From diphenyldichlorosilane Kipping [6] was able to isolate the simple diphenylsilandiol, and both cyclic and linear condensation products of the following formulae:

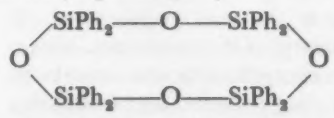
$HO.SiPh_2.O.SiPh_2.OH$
Tetraphenyldisiloxandiol (m.p. 113° C)

$HO.SiPh_2.O.SiPh_2.O.SiPh_2.OH$
Hexaphenyltrisiloxandiol (m.p. 112° C)

$HO.SiPh_2.O.SiPh_2.O.SiPh_2.O.SiPh_2.OH$
Octaphenyltetrasiloxandiol (m.p. 128·5° C)



Hexaphenylcyclotrisiloxane
(m.p. 188° C)

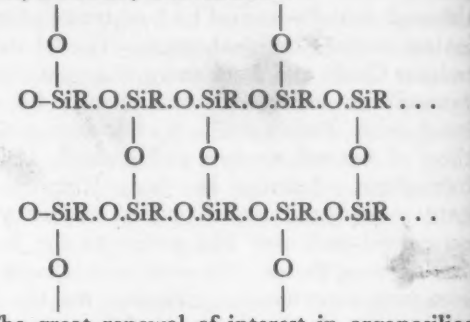


Octaphenylcyclotetrasiloxane
(m.p. 201° C)

Yet more complex compounds with longer chains and larger rings must account for the glue-like products into which the simpler compounds readily pass when heated. Intermediates of type $RSiX_3$ are hydrolysed to organosiloxanols:

$$R.SiX_3 + 2H_2O = R.SiO.OH + 3HX$$

These are usually amorphous powders or hard, brittle solids; many have no definite melting-point, and some are quite infusible. They consist of condensation products of varying degrees of complexity derived from the hypothetical organosilantriols ($RSi(OH)_3$), and may be of linear, cyclic, or cross-linked structure, the end-product of the dehydration process being cross-linked, insoluble, and infusible:



The great renewal of interest in organosilicon chemistry follows naturally from the intensive study and commercial development of high polymers. Here is a new class of highly condensed materials possessing a considerably greater degree of thermal stability than the accepted plastics. Their basic structure of recurrent siloxane units, analogous to that of the silicates, suggests that they may be good insulators of electricity. It would appear that this line of thought was being pursued by Russian investigators at an early stage, for in 1932 Dolgov [7] published a review of previous work on organosilicon compounds, and in 1935 Shtetter [9] patented the production of substituted chlorosilanes from silicon

[1] The system of nomenclature employed is that of R. O. Sauer [8].

etrachloride and the simpler unsaturated hydrocarbons such as acetylene and ethylene. A few years later, several papers were published by Andrianov [10] and by Kotow [11] on the condensation products of the alkyl and arylsiloxanols (R.SiO.OH) and their application as heat-hardening resins. The products were too brittle for use alone, but when mixed with drying oils they gave satisfactory insulating varnishes.

In the United States, work on organosilicon compounds has been highly competitive. Initially there were three independent groups, represented by the Corning Glass Works, the Mellon Institute, and the General Electric Company, but at a later stage the first two and the Westinghouse Electric Corporation joined forces. Dr E. C. Sullivan, head of the Corning research department and discoverer of 'Pyrex' glass, desired a heat-resistant resin which could be used for impregnating glass fabric to give a flexible electrical insulation, and in 1931 Dr J. F. Hyde was assigned the task of making such a resin from organosilicon compounds. At the Mellon Institute, Dr G. R. McGregor went a long way towards an independent solution of the same problem before collaborating with Hyde. Other useful products were discovered, and it soon became necessary to begin manufacture. For this purpose the co-operation of the Dow Chemical Company was sought, and in 1943 the Dow-Corning Corporation was formed to manufacture and develop the new organosilicon products. These were dubbed 'silicones,' a term originally used by Kipping for the analogues of ketones. The Dow-Corning plant is based on the Grignard method of synthesis, and has a monthly output of 40–50 tons of various silicone products.

The research and development programme of the General Electric Company has been most energetically carried out by a large group of competent research workers, notably by Dr E. Rochow, and this powerful concern will shortly be in a position to manufacture a complete range of silicone products. So far, production has been on a pilot-plant basis with a monthly output of about two tons. Of major importance has been the discovery of a new method [12] for producing organosilicon intermediates. This consists in bringing the vapour of an alkyl or aryl halide into contact with an intimate mixture of silicon and copper or silver at an elevated temperature:

$$Si + 2CH_3Cl \xrightarrow{Cu} (CH_3)_2SiCl_2.$$

The catalytic action of copper and silver is thought to be connected with the transitory formation of their organocompounds [13]:

$$CH_3Cl + Cu \longrightarrow CH_3CuCl.$$

The process is particularly effective with methyl chloride at 280–300° C, and leads to a complex mixture of methylchlorosilanes, chief of which is dimethyldichlorosilane (b.p. 70° C). Methyltrichlorosilane (b.p. 66° C) is also present in notable proportion, while trimethylchlorosilane (b.p. 57° C) and methyldichlorosilane (b.p. 42° C) are minor constituents. In the preparation of certain silicone products it is necessary to employ highly purified intermediates so that the degree of cross-linkage may be kept under close control. Owing to the proximity of their boiling-points, the methylchlorosilanes can be separated only in highly efficient fractionating columns (80–100 theoretical plates). This new synthesis is well adapted to large-scale production, and it may be expected that manufacturing costs will be lower than with the Grignard process. Unfortunately the direct synthesis is not uniformly successful, so that wherever it proves impracticable or uneconomic the Grignard method will still hold sway.

FIGURE 1 – *Professor F. S. Kipping, F.R.S.*

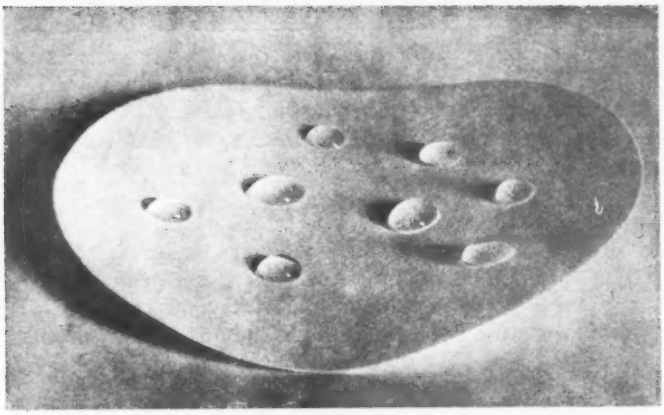


FIGURE 2 (*above*)–*Water-repellent filter paper. The filter paper was exposed for fifteen seconds to the vapour of methyltrichlorosilane and then to gaseous ammonia. The water drops are not absorbed and do not wet the paper, which retains its strength and permeability to gases and most other liquids.*

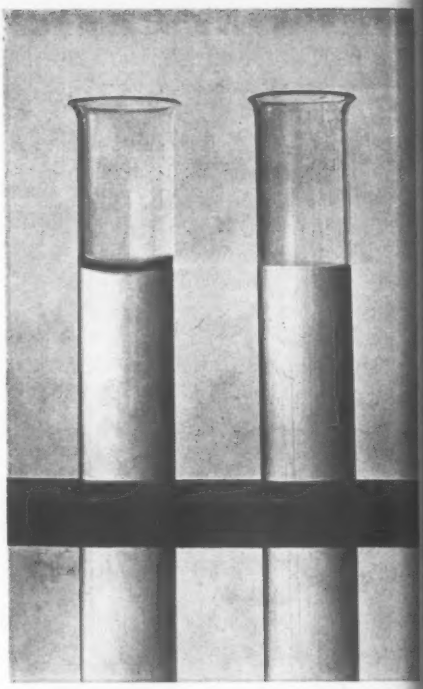


FIGURE 3 (*right*)–*Glass tubes containing water. On the left is a normal clean test tube, showing the meniscus, characteristic of a liquid which wets glass. The right-hand tube is a similar tube, the inside of which has been in brief contact with liquid dimethyldichlorosilane and then thoroughly cleansed with alcohol and ether. The water surface is flat because the glass is not wetted.*

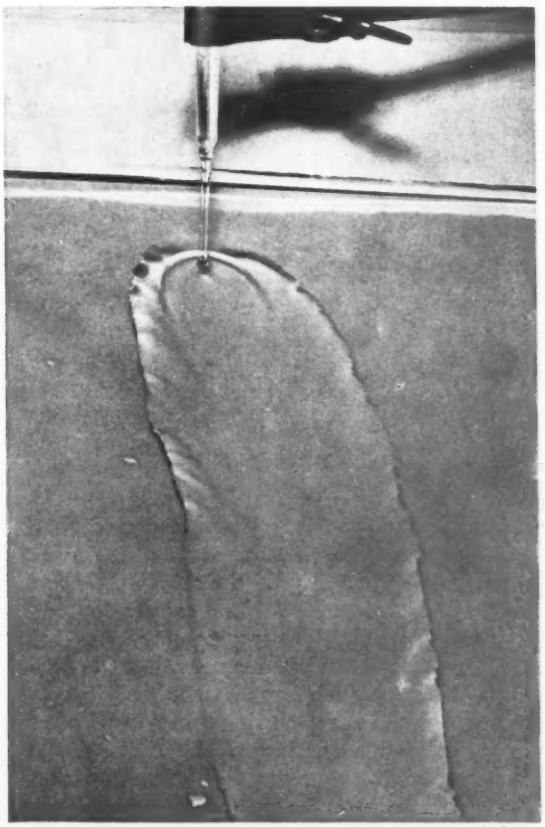


FIGURE 4*a* – *Water flowing down a clean glass plate inclined at 35°. The thin and wide spread shows that the glass is thoroughly wetted. The shape of the moving water film remains substantially unaltered.*

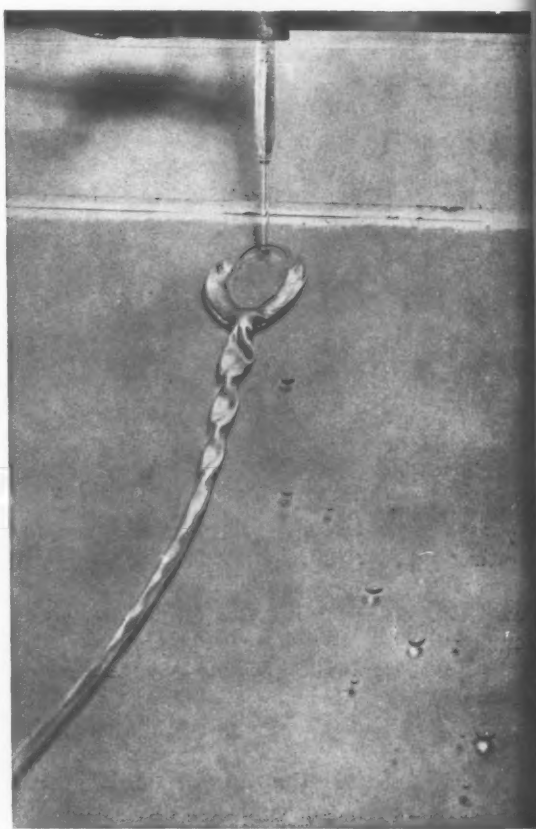
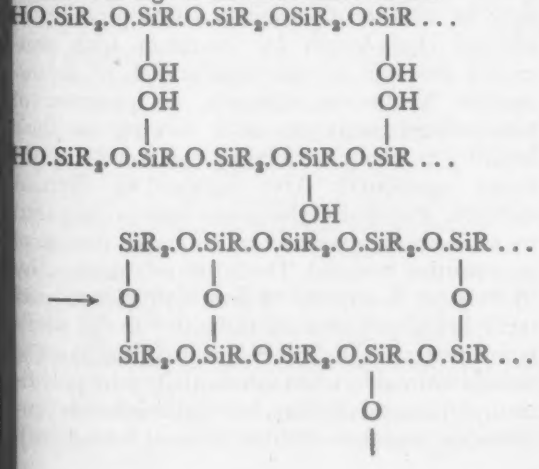


FIGURE 4*b* – *Water flowing down a similar glass plate which has been previously rendered water-repellent by contact with liquid dimethyldichlorosilane. The water runs down the glass with a minimum area of contact, and by continually changing its path produces an effect reminiscent of the violent movement of a serpent.*

An interesting property of certain organosilicon compounds is their ability to produce water-repellent surfaces on glass and ceramics, and to waterproof materials such as paper and cotton [14] which consist chiefly of cellulose (see figures 2, 3, 4). This result may be achieved by a short exposure to the vapour of dimethyldichlorosilane. It is believed that this material reacts with superficial hydroxyl groups and metallic atoms to give a chemically bound, water-impermeable layer of dimethylsiloxane groups. In the case of cellulosic materials it is necessary to neutralise immediately afterwards in order to prevent the harmful action of hydrogen chloride. An alternative and less objectionable method is to impregnate with a liquid polydimethylsilicone and then to subject to a suitable heat-treatment. This is particularly suitable for ceramics, and was employed to safeguard radio and radar equipment against failures due to the deposition of water films on such ceramic parts as coil formers, the bases of high-frequency transformers, and wire-wound resistors.

Paper filters waterproofed in this way were fitted to certain respirators to prevent damage by immersion. It is to be noted that these water-repellent surfaces are eventually obliterated by films of grease and dust. Great care must therefore be taken in their preparation and subsequent treatment; they must not be handled, and should be used only under conditions which substantially preclude contamination.

Silicone resins [15] are produced essentially by condensing a chain-forming intermediate with one capable of cross-linkage; they consist of long-chain molecules which possess a controlled amount of hydroxyl groups. Dissolved in toluene they form viscous varnishes which pass into insoluble coatings when dried and baked.



The baking temperatures are comparatively high (175–250° C), and thereafter the resins may be maintained at 175–200° C for long periods without depreciation. For any given pair of intermediates the amount of cross-linkage must be kept within narrow limits, outside of which the products are of no value as coating materials. This range can be found only by trial, and it will be apparent from the variety of organic radicals that may be present that a great deal of experimentation is necessary to find resins with the desired combination of properties. Those now available have been selected for specific applications. There are insulating varnishes for coating wires, and resins for impregnating glass cloth. Layers of resin-impregnated glass fabric may be bonded together, by heating under pressure, into strong panels or tubes. Other resins may be mixed with thermally stable pigments to give heat-resistant paints and enamels.

The principal object in developing silicone resins was to provide improved forms of insulation for electrical machines such as motors, generators, and transformers [16]. Conventional insulations involve the use of organic varnishes and drying oils, paper, and cotton, and are relatively short-lived when used in heavy-duty machines, particularly those which operate at high ambient temperatures and with occasional periods of overload. Class A insulation, comprising organic varnishes, paper, and cotton, is limited to 100° C, as determined by the resistance method. If the paper and cotton are replaced by glass or asbestos cloth (Class B), the limit is raised to 120° C. From a series of accelerated tests [17] at temperatures up to 300° C it is concluded that insulations based on silicone resins, glass, and asbestos cloth, mica, etc., will permit a limit of 160° C with normal expectations of life. This means a greater degree of freedom for the designer. Silicone insulation is not only heat-resistant but resistant to water and aqueous solutions, and so should find application in mines, and in factories where corrosive chemicals are handled.

The need for a heat-resistant substitute for the rubber insulation on electrical leads has been met by the truly remarkable silicone rubber [18]. This differs from all other rubber-like materials in that its molecular backbone contains no carbon atoms, since it consists of a long chain of dimethylsiloxane groups:

$$HO.Si(CH_3)_2.O.Si(CH_3)_2 \ldots$$
$$O.Si(CH_3)_2.O.Si(CH_3)_2.OH$$

It is produced from the hydrolysis product of

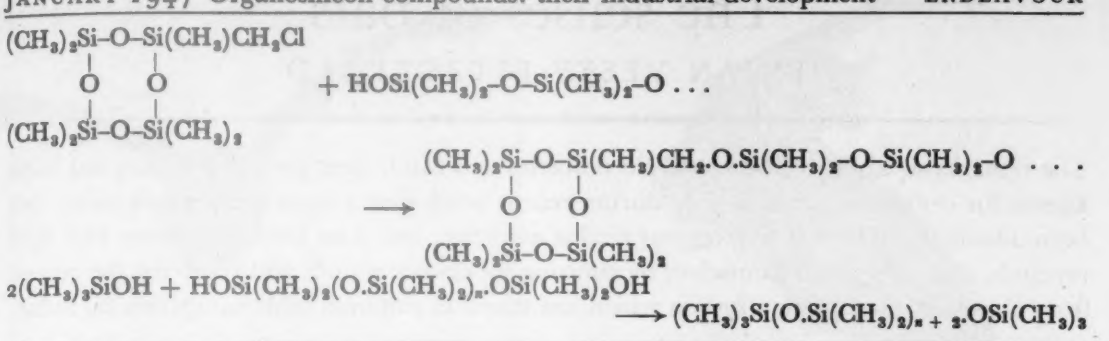
substantially pure dimethyldichlorosilane by heating with hydrochloric acid and the active metallic chlorides, and resembles a translucent gum or sticky jelly. To develop rubber-like properties, cross-linkages must be established between the long-chain molecules by some process of vulcanization, but, as it is saturated, the conventional vulcanization with sulphur is not possible. The method used appears to be one of controlled oxidation, and is probably induced by heating with an organic peroxide. The gum is compounded with suitable proportions of inorganic fillers and vulcanizing agent, and is then moulded, pressed, or extruded at about 150° C. This develops dimensional stability, but the full strength is not attained until after a lengthy cure at 250° C. The tensile strength is lower than that of most other rubbers, being only about 650 pounds per square inch, and the maximum elongation varies between 100 and 300 per cent. The tear-resistance is also poor, but can be improved by incorporating a fabric. Silicone rubber has outstanding heat and oxygen resistance, and has been used extensively as gasket material for joints exposed to temperatures up to 200° C or more.

The erection of the Dow-Corning plant in 1943 was due to a large demand for a material capable of sealing the ignition harnesses of aircraft engines against corona discharge. This trouble is encountered at high altitudes, and may quickly lead to engine failure owing to destruction of insulation. It was found that a grease made by hydrolysing a mixture of silicon tetrachloride, dimethyldichlorosilanes, and methyltrichlorosilanes was eminently suitable for this purpose. It is a colourless, translucent grease which does not change in consistency over the temperature range −40° C to above 200° C, and although its electrical resistance is high it does not form an insulating layer at the disconnectable junctions employed on ignition harnesses. The grease is not only without harmful action on rubber and synthetic insulations but has proved to be a good lubricant and preservative for these materials. When electrical discharge takes place in the grease some carbon is formed, but the principal decomposition product is silica, and so tracking is not as serious as with ordinary organic insulators. The grease was applied to disconnectable junctions and to spark-plug wells in such a way as to exclude air from them. At the same time ingress of moisture was prevented, and so short-circuits due to water films were prevented. During the war silicone ignition-sealing grease contributed in no small way towards the safe operation of Allied aircraft at high altitudes.

The grease found further application in radio and radar equipment, and was used as a lubricant for the shafts and other movable parts of rotating antennae and for the swivel joint in the oxygen supply line to rotating gun turrets on aircraft. It has also been used as a lubricant for the rubber bags used in the low-pressure moulding technique with contact resins. A high-vacuum grease is particularly useful on account of its low vapour pressure, high film strength, and ability to wet all types of surfaces. Special greases thickened with carbon black and with metallic soaps are suitable for lubricating high-speed bearings that must operate at temperatures as low as −75° C or as high as 150° C.

On hydrolysis, dimethyldichlorosilane gives a variety of condensation products of dimethylsilandiol, some being cyclic like hexamethylcyclotrisiloxane (m.p. 65·5° C, b.p. 135° C), while others are linear. Wide variation of molecular complexity is possible, and hence the liquid products cover a wide range of boiling-point and viscosity [19]. These silicone fluids possess many interesting and useful properties; for example, owing to their low molecular cohesion [20] the change of viscosity with temperature is remarkably small. They have high electrical resistance and low power factor up to 10^7 cycles per second. Various artifices are employed to modify and extend the range of available liquids; the viscosity may be increased by heating in air, by boiling with hydrochloric acid, and by condensation with boric anhydride. Other methods are to condense with a lightly chlorinated polymer or with trimethylsilanol (see top of page 35).

In this last process [21] it is claimed that any given condensation product of dimethylsilandiol may be substantially converted into products of selected chain-length by treatment with controlled amounts of trimethylsilandiol, or its anhydride hexamethyldisiloxane, in presence of concentrated sulphuric acid. Owing to their inability to condense further, these end-stopped linear compounds have outstanding thermal stability. Polydimethylsiloxanes may be prepared by an interesting method which avoids the use of pure starting material. The brittle gels obtained by hydrolysing a mixture of dimethyldichloro- and methyltrichlorosilanes are submitted to dry distillation, preferably in the presence of a strong base like sodium hydroxide, when substantially pure polydimethylsiloxanes volatilize, leaving the infusible condensation products of methylsiloxanol behind [22].



Their combination of low viscosity-temperature gradient, wide fluid range, and high compressibility makes certain of these liquid products eminently suitable for use in sensitive hydraulic systems, damping devices, and shock absorbers. Others are effective as mould-release agents, fibre lubricants, and water repellents, and certain exceptionally stable high-boiling products are suitable for use in diffusion pumps, high-temperature baths, and thermally responsive devices. Silicone fluids are remarkably effective in reducing the foaming tendency of hydrocarbon oils, even at dilutions as low as 1 in 10^6.

When delivering the Bakerian lecture to the Royal Society in 1937 Kipping reviewed the organic chemistry of silicon, and concluded with the following words:

> 'Most, if not all, of the known types of organic derivatives of silicon have now been considered, and it may be seen how few they are in comparison with those which are entirely organic; as, moreover, the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem to be very hopeful.'

That events have proved otherwise is no reflection on his judgment. Doubtless the experimental difficulties with which the subject bristles weighed heavily in the balance, but fortunately human endeavour is cumulative: each new worker starts with vigour and enthusiasm from the advanced bases provided by his predecessors. With characteristic faith, vision, and capacity for intensive work, American investigators and industrialists have been quick to translate the academic results of an English chemist into a fascinating new field of chemical technology. The debut of silicones has been brilliant and full of promise, but their present high cost[1] places them in the luxury class of chemicals. So far, their employment has been restricted to applications in which a valuable advantage can be secured only by making use of their unique properties. Future development must depend on their ability to compete with other new materials on a cost basis, and it may be anticipated that much attention will be given in the near future to the possibility of devising new and cheaper methods for producing the fundamental intermediates.

[1] On the basis of their silicone content, the cost is about seven dollars per pound.

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The senses of bats

BRIAN VESEY-FITZGERALD

The remarkable ability of bats to avoid obstacles and catch their prey in the dark has been known for centuries, but it is only during recent years that a convincing explanation has been advanced. There is now a great deal of evidence, based on both laboratory and field research, that bats guide themselves by emitting supersonic sounds and receiving the echoes from objects in their path, a system which has much in common with navigation by radar.

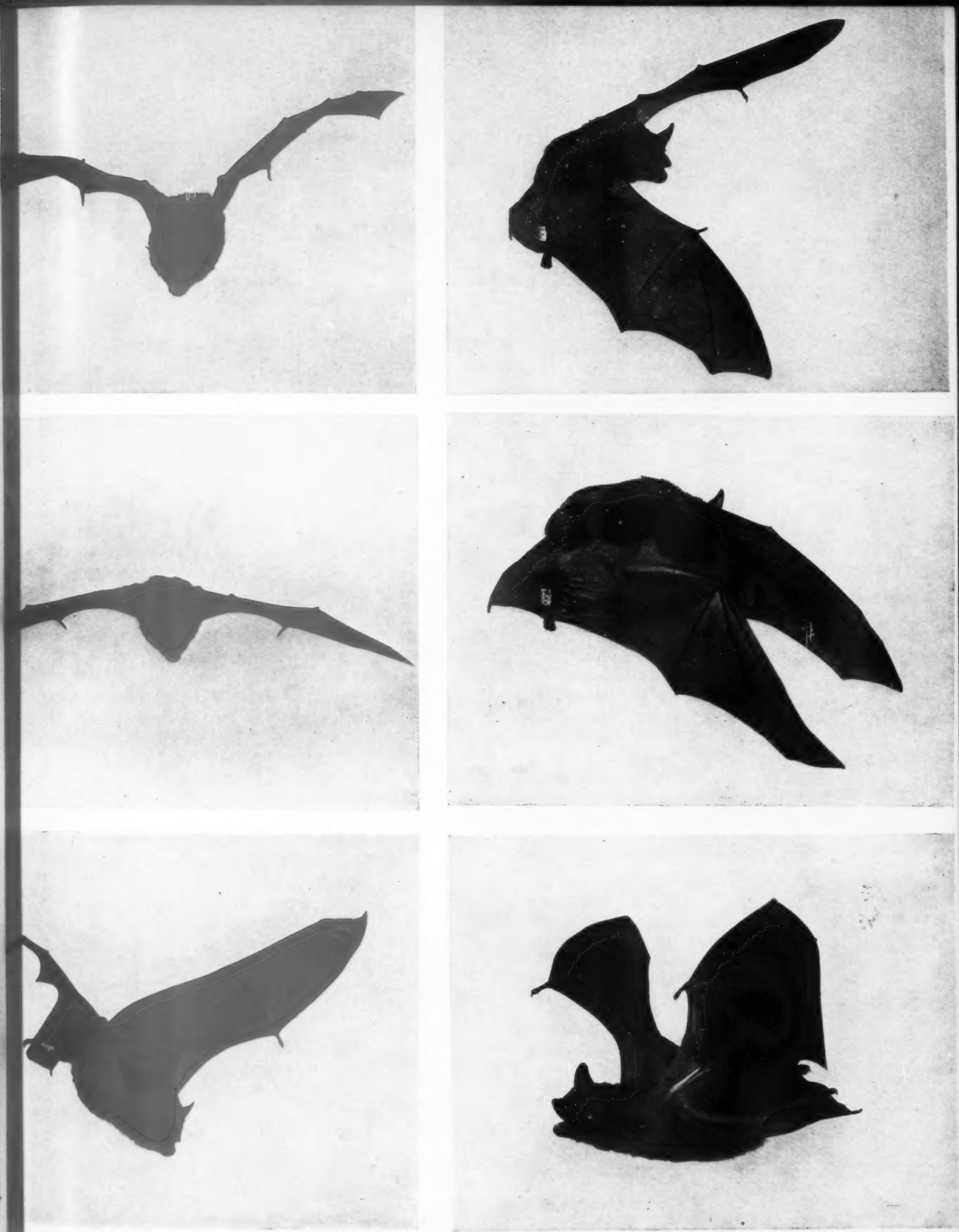
Of all the many problems which bats set for the inquiring naturalist, none has been more puzzling than that presented by their flight at night: the way in which they catch the insects upon which most of them feed (in the case of British bats, upon which *all* of them feed) without colliding with objects in their path. The flight of bats is rapid and the course erratic, frequently through thick woods or the narrow winding passages of caves, often in total darkness. It has always seemed unlikely that animals with such small eyes could see well enough in the dark to fly in such surroundings without mishap. Many experiments have been tried with captive bats to demonstrate their ability to avoid obstacles which they could not see. Towards the end of the eighteenth century the Italian scientist, Lazzaro Spallanzani, found that bats which he had blinded could fly about a room, avoiding the walls, the furniture, and silken threads stretched across their path. A Swiss scientist, Louis Jurine, confirmed this and made the additional discovery that bats lost their ability to avoid obstacles when their hearing was interfered with. Cuvier poured scorn on these findings, and they were forgotten for a century and a half. All that was remembered was that a blinded bat could fly perfectly surely. But the uncanny ability remained, and all sorts of theories were advanced to account for it. It was suggested, for example, that bats were very sensitive to changes in atmospheric pressure.

Then, in 1920, Professor Hartridge suggested that bats when flying in the dark were probably able to ascertain the position of obstacles by means of supersonic sounds emitted by the animals and reflected to their ears. Twenty years later, after the development of radar as an operational system, Griffin and Galambos working in America were able to prove him correct.

Both radar and sonar are, of course, founded on the same fact, namely that if a short burst of energy is sent out and the time taken for the echo to come back is noted, then, if the speed at which the energy travels is known, the distance of the object can be accurately calculated. Moreover, by sending the energy down a narrow beam the bearing of the object can be accurately determined. In radar the energy used is in the form of electromagnetic waves; in sonar (the method by which the depth of water is measured) ordinary sound waves are used. In their direction-finding bats use not audible sound waves, but, as Hartridge suggested and as Griffin and Galambos have proved, supersonic waves. The range of frequencies that a normal human being can hear is from about 16 vibrations a second to about 30,000 a second. Middle C is 256 vibrations a second. The range of frequency of the supersonic waves used by bats is from about 25,000 to 70,000 a second, and is thus mostly above the limit of human hearing.

Griffin and Galambos began their work by confirming that blindfolded bats are able to fly surely. They then confirmed Jurine's discovery that if the hearing of a bat is impaired it is unable to avoid obstacles when flying. Indeed, they found that a bat with both ears covered is most reluctant to take wing at all, but that a bat with one ear covered will fly with moderate success, though it will be unable to avoid all obstacles. These simple experiments indicated that bats are made aware of the position of obstacles which they cannot see by means of sound waves reflected from them. They then covered the noses and mouths of their bats, but left the ears uncovered, and found that again the animals were unable to fly with certainty. They thus proved that the sound waves reflected by objects must be produced by the vocal apparatus of the bats themselves.

Their further experiments were conducted with the aid of an electronic apparatus known as a supersonic analyser. This consists essentially of



ES 1–3 (*read down*)–*The wing action of a bat in level flight, owards the camera. Bats make between fifteen and twenty such of the wing a second, and fly at about ten miles an hour.*

FIGURES 4–6 (*read down*)–*Level flight broadside to the camera. Bats fly by raising the wings partly folded and bringing them sharply down and forward. Note that in all these photographs the mouth is held open.*

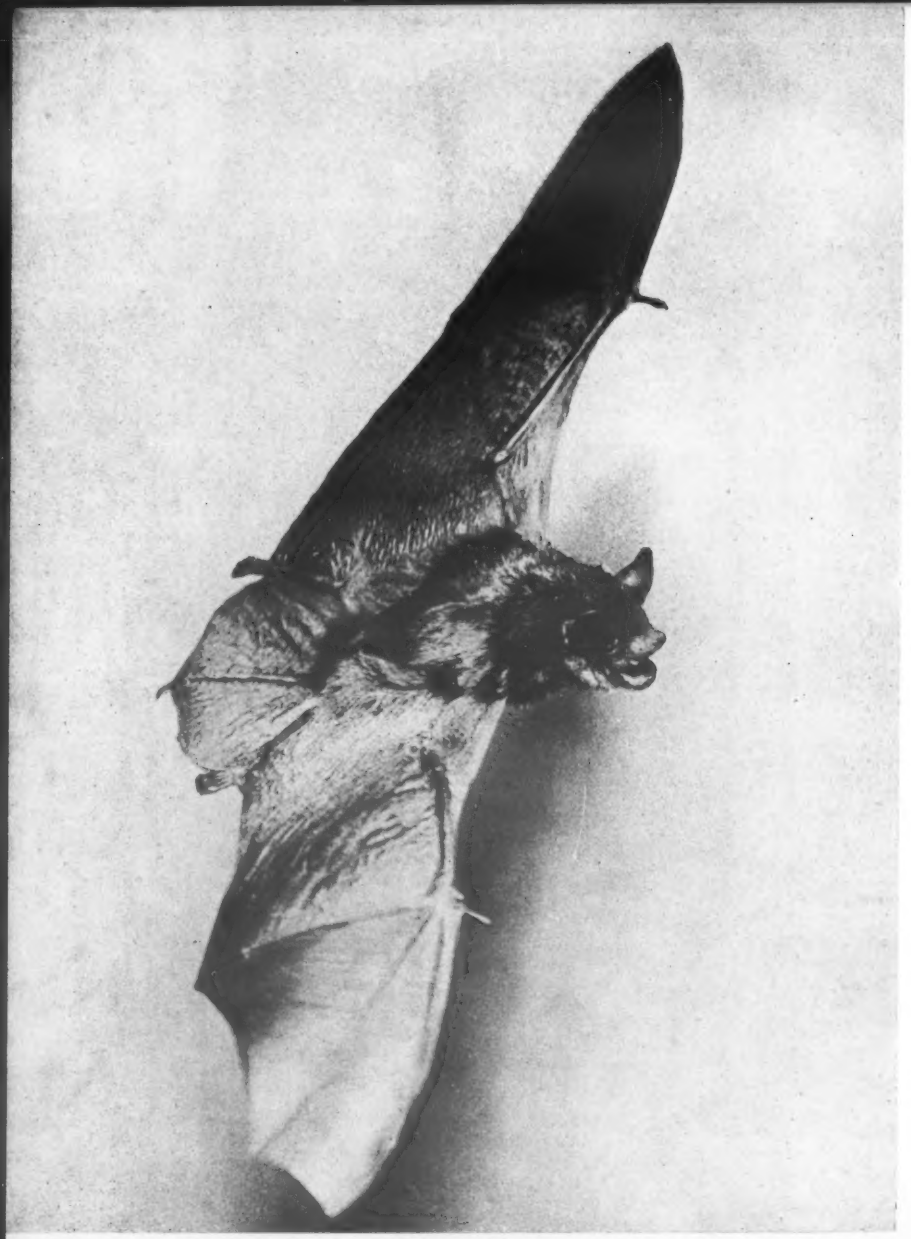


FIGURE 7 – *Warned by the echo, a bat banks sharply to avoid a wall. How close it has come without accident is shown by the shadow.*

FIGURE 8 – *Swooping to alight. Note the depressed interfemoral membrane. All these photographs were taken at* [illegible] *sec.*

a microphone sensitive to supersonic vibrations, a magnifier which amplifies them and converts them to vibrations of a lower frequency, and a recorder which traces a graph on paper when supersonic sounds are received. The analyser measures the frequency of any supersonic vibrations it may pick up. By means of this instrument it was discovered that bats make supersonic sounds at frequent intervals almost all the time. The frequency of the vibrations varies, of course, but it is most usually about 50,000 a second, and at this pitch each squeak lasts for a little less than one two-hundredth of a second.

Now, it is evident that the more frequently squeaks are emitted the fuller the information received. It has been proved that a bat at rest emits a supersonic squeak about ten times a second, but that as soon as it takes wing the rate goes up to about thirty a second. That was to be expected, since a bat on the wing obviously needs more information than a bat at rest. Griffin and Galambos further found that the closer a bat approached an obstacle the faster became the rate of squeaks, rising to fifty and sometimes even to sixty a second, and dropping to normal as soon as the obstacle was passed. The rate of squeak is, of course, governed by the distance from the object, for there must be time for the echo to come back before the next squeak is sent out.

The supersonic tone is not the only sound produced by bats. In addition to the supersonic squeak, which cannot be heard by human beings, they produce three other kinds of sound: (1) the ordinary voice, which is the flight call, and which Hartridge has named the signalling tone; (2) a buzz, which is audible if one is quite close to the animal; and (3) a click, which is usually audible at a distance of several feet. I am not competent to say whether the buzz differs in any way with the species; it sounds exactly the same to me whether emitted by a Serotine (*Eptesicus serotinus*) or a Pipistrelle (*Pipistrellus pipistrellus*), nor can I distinguish any difference between the clicks emitted by the different species. The flight calls, however, are quite distinct. It is possible to distinguish between the species on the wing by means of their flight calls (it is also possible with practice to distinguish between the types of flight), and I have elsewhere attempted to translate the differences between the calls of the various species to paper. It has been shown that the buzz and the click are accompanied by the supersonic tone. In the case of the click there is a single short burst of supersonic energy, but in the case of the buzz there is a continuous evolution of the interrupted supersonic tone. The flight call, however, may be produced by itself or it may be accompanied by the supersonic tone. Some bats, notably the Lesser Horseshoe (*Rhinolophus hipposideros*), have a considerable vocabulary of ordinary sounds, whereas others, notably the Whiskered (*Myotis mystacinus*), scarcely ever make a sound of this sort. I have never heard the Whiskered utter a sound on the wing, and of the many I have kept in captivity only a few have uttered faint grunts, and those very occasionally, when at rest.

How these four different types of sound are produced is not yet clear, but examination of the vocal organs of bats shows that they are very different from those of other animals. The larynx, which in most animals is built of cartilage, in bats is made of bone and is comparatively a massive structure with large and powerful muscles. The strength of the bat's larynx and its small size are obviously well adapted to the production of supersonic sounds, for there must be tremendous energy in the supersonic squeaks as compared with the audible squeaks. The higher the note and the greater the frequency, the greater the energy.

Though it is not yet known exactly how the supersonic vibrations are produced, it is known how the bat avoids hearing the squeak. It is, of course, essential that only the echo should be heard by the bat. The same difficulty had to be overcome in radar transmission. In order to ensure that only the echo is picked up by the receiver, this is suppressed while the transmitter sends. Something of the same kind happens in the bat when emitting the supersonic tone. Griffin and Galambos found that while the squeak is being made a muscle in the ear contracts momentarily, shutting off the squeak, and permitting only the echo to be heard.

Bats are not the only creatures with the power of echo-location. The tapping of Blind Pew's stick is an example of the same process, and many blind human beings develop what appears to be an uncanny ability to move about without striking obstacles. Nor are bats the only creatures able to hear supersonic vibrations: dogs, for example, are often trained on the Galton whistle. But so far as is known at present bats are the only creatures that emit supersonic vibrations and guide themselves by the reflections. This important discovery, however, still leaves unanswered many questions about the behaviour of bats, and, as is the way with important discoveries, poses a number of fresh problems.

FIGURE 8 – *Swooping to alight. Note the depressed interfemoral membrane. All these photographs were taken at 1/1000 sec.*

FIGURE 7 – *Warned by the echo, a bat banks sharply to avoid a wall. How close it has come without accident is shown by the shadow.*

Invariably the first question that is asked is: Why do not the bats become confused between the echoes from their own squeaks and the echoes from the squeaks of their neighbours? It might be thought that with a large number of bats of the same species together in a cave or in the roof of a church, and all uttering supersonic squeaks, confusion would be inevitable. But it must be remembered that supersonic squeaks do not travel far, for their energy is quickly dissipated in the air. It has been shown that the supersonic squeaks of bats travel only about fifteen feet, and that they are able to give a useful echo only up to about twelve feet. In other words, provided that the bats are not crammed close together, there is very little likelihood of confusion. But, as everyone with any field experience of bats knows, they very often are crammed close together, yet there is no confusion. It seems evident that there is a difference in the frequency of the vibrations made by each bat. A very slight difference in frequency would be sufficient to enable each bat to recognize its own voice.

There remain a number of problems to which no answer has yet been given. Firstly, do bats emit the supersonic squeak through the mouth or the nose, or both? All the British bats are insect-eaters, and all, with the possible exception of the Barbastelle (*Barbastella barbastellus*), habitually fly with their mouths open. Furthermore, all the British bats capture their prey while in flight, and most of them take flying insects. What happens when the bat closes its mouth on catching an insect? Does echo-location cease (in which case the bat must fly blind) or does it continue through the nose? We do not know. In the Greater Horseshoe (*Rhinolophus ferrum-equinum insulans*) the epiglottis does not open into the back of the mouth as in most animals, but is projected up into the roof of the mouth, fitting into the rear opening of the nasal passages. It is not fixed in this position, and can probably be withdrawn, but the arrangement suggests that the supersonic squeaks, in the *Rhinolophidae* at any rate, are emitted through the nose, and this suggestion receives additional support from the extraordinary skin development on the muzzles of these bats. While the purpose of this appendage, which in some species attains an astonishing complexity, is not known, it has been suggested that it is concerned with directing the squeak into a narrow beam so that the bat's knowledge of its position is greatly increased. Be that as it may, I have no doubt from long personal observation that the Horseshoes have a much finer appreciation of position than other British bats, and especially is this so in the case of the Greater Horseshoe. Indeed, this species is quite uncanny in its judgment of distance. Bats normally hang head downwards, suspended by the toes. It is the usual practice for bats to land head upwards and then to shuffle round until they can get a grip with the toes, but the Greater Horseshoe is accustomed to turning a somersault in the air and gripping straightway with the toes, landing, in other words, in the head-downward position. Very rarely indeed have I seen a bat miss its hold, and there appears to be no slackening of speed as the resting-place is approached. Some of my captive Greater Horseshoes used to sleep under a sideboard, and when they were hanging there was little more than a couple of inches clearance from the floor, yet they would fly under the sideboard, turn their somersaults with absolute certainty, and hang by the toes. And many, many times have I watched this acrobatic performance when they have been hanging from picture-rails and so forth.

There is a marked difference in the structure of the ear in the *Rhinolophidae* and in the *Vespertilionidae*. In the former the pinna is comparatively simple in build, but in the bats without nose-leaves the ear is a much more complex structure, characterized by a great development of a lobe known as the tragus. This is especially well seen in the Long-eared (*Plecotus auritus*), in which species it stands up like a second pinna. It has been suggested that the tragus is in some way connected with echo-location, and the fact that the bats with nose-leaves have no tragus while the bats with the tragus have no nose-leaves is surely significant. It would appear that the two developments must in some way perform similar functions.

It is, I think, noteworthy that the Long-eared, in which there is such a marked development of the tragus, is in comparison with other bats of the same group a master of flight in confined quarters. Most bats, when flying to their feeding-grounds, do so at a considerable height; the Long-eared does so very close to the ground, often at a height of no more than a few inches, and the flight is fast, direct, and confident. Furthermore, the Long-eared captures comparatively few insects in flight, preferring to pick them off the leaves of bushes and trees, a habit which entails the nicest judgment of distance.

Two other British bats, Natterer's (*Myotis nattereri*) and the Whiskered (*M. mystacinus*), have the habit of picking their prey from foliage rather

than taking it in flight. Natterer's is fairly impartial, but the Whiskered very rarely captures a flying insect, preferring to search the hedgerows and fences, especially for spiders, of which it is inordinately fond. Both species have a well-developed tragus, and in both, but more particularly in Natterer's, there is a marked development of the glandular pads on the face.

How bats find their prey is a mystery that has not yet been solved. It is certain that they cannot find it by sight, and there does not seem to be any evidence that their powers of scent are particularly acute. How, then, does the Noctule (*Nyctalus noctula*), flying high and fast, find its prey? If you throw a pebble into the air beneath a hawking Noctule, the bat will dive on to it, swerving away from it at the very last moment without touching it. Attach a fly to a long line and make casts into the air while bats are hawking and you will have them diving at the fly, but it is very unlikely that you will catch one. Daubenton's bat (*Myotis daubentonii*) is sometimes caught on the flies of anglers, but almost always by the wing. I do not think that there has been a single instance of the bat being caught by the mouth, which suggests that at the last moment (but too late to avoid contact altogether) it has realized its mistake. All this suggests that the supersonic squeak sends back an echo from anything flying into or across the path, but it does not explain how the bat knows that that something is worth investigating. Yet I have never seen one bat dive at another, even when there have been many flying at random in a confined area. Nor does it explain how the Long-eared and the Whiskered know that there is an insect or a spider on what their echo-location must have told them is an obstacle to avoid. Yet in a long experience of Whiskered bats, I have not seen one hit a fence or make fruitless visits along a hedge.

One would be inclined to say that the supersonic tone was even more selective than we know it to be were it not for certain things that field experience has brought to notice. I have seen bats of different species collide in mid-air—on one occasion a Noctule with a Serotine (and both animals were killed), and on another occasion a Pipistrelle with a Barbastelle (when the Pipistrelle was killed). These accidents happened during the evening hawking, and one can only suppose that at the time echo-location had stopped, possibly because both animals had captured insects and their mouths were closed.

Field experience shows too that there are times when echo-location does not function at all. I have caught many bats by netting their dens of a summer night. At one time, anxious to discover whether bats flew at night or not—it was at that time thought that they had an evening and a morning flight only—I made a number of all-night watches at dens of Noctule, Whiskered, Pipistrelle, Serotine, and Natterer's, and, after the bats had left the hole for the evening flight, netted the entrance. I caught many bats (and at almost all hours of the night) in the nets, trying to get back to the holes. At that time nothing was known about supersonic vibrations in connection with bats, and I did not think that there was anything odd about it. But in the summer of 1946, realizing that the supersonic tone should have warned them of an obstruction, I repeated the process at dens of Noctule, Whiskered, Daubenton's, and Serotine, with the same result. The bats appeared to be quite unaware that there was an obstruction and flew straight into the nets. Later I covered the entrance hole to a Noctule den with thick brown paper, and even this did not seem to be indicated to the bats, which flew straight into it. Before returning to their den Noctules fly round the tree and in and out among the branches with never a false movement, yet they are unaware of an obstruction at the very entrance to their sleeping-quarters. It seems evident that echo-location, for some reason, is shut off at that moment.

On the other hand, it seems to operate to some extent during hibernation. Everyone who has entered a hibernaculum of bats must have noticed the tremor that goes through the sleeping creatures at the first presence of a stranger. They are asleep, and incapable of movement, but there can be no doubt at all that they are aware.

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The meaning of resonance in quantum chemistry

C. A. COULSON

The system of equations known as quantum mechanics is unquestionably one of the most important discoveries in the history of science. A particularly interesting chemical application of it is the theory of resonance. This theory, of which a general account is given here, provides a formal and logical explanation of the properties and reactions of a very diverse range of substances. Of outstanding interest is the close similarity between the resonance structures for benzene and those advanced by Kekulé as long ago as 1865.

Resonance in quantum chemistry is a comparatively recent idea, which owes both its birth in 1933 and its early development almost entirely to the work of Linus Pauling in the United States. It is concerned with the way electrons behave in molecules. But before we can understand this we must go back to the individual atoms out of which molecules are formed and ask how the electrons move there; after that, we can discuss their behaviour in simple molecules, and this will lead us almost immediately to the concept of resonance.

The important point about the motion of an electron in an atom is that, since the electron is so very tiny and moves so very fast, we can never measure exactly where it is, and can at best get a kind of blurred pattern. This is quite understandable when we realize that the average velocity of an electron in an atom is at least two million miles per hour, and its orbit is less than one hundred-millionth of an inch across. The shape of this pattern may be calculated mathematically from the so-called Schrödinger Wave Equation. These calculations are quite elaborate, and for our present purposes it is sufficient to say that, although we can never tell exactly where an electron is, we can state that there is a very high probability (e.g. 95 per cent.) that it is within a certain definite volume. Different electrons in an atom will have volumes of different shapes, which they may be said to 'occupy.' In figures 1 and 2 we show these boundary contours for the electrons in hydrogen and oxygen atoms. In hydrogen the one electron lies within a spherical volume of diameter roughly 10^{-8} cm. In oxygen, with eight electrons, two of them (the inner 1*s* or K-shell electrons) have volumes of the same kind but only one-eighth as large; two more (the 2*s* electrons) have spherical volumes of about the same size as in hydrogen; the remaining four (2*p* electrons) lie within boundaries somewhat similar to a dumb-bell or a cottage-loaf in shape. The normal oxygen atom could be pictured as a superposition of all these patterns.

The 'shape' of a molecular electron in a diatomic molecule is not essentially different from

FIGURE 1 (*left*) – *Boundary contour for hydrogen atom*

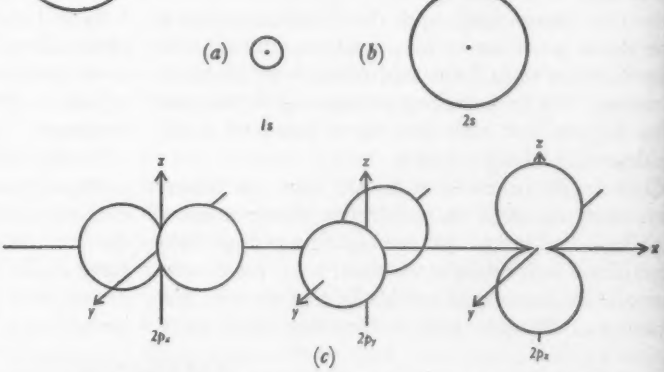


FIGURE 2 – *Boundary contours for oxygen atom. An oxygen atom has its nucleus at the origin and:*

(*a*) *Two electrons in a 1s volume.*

(*b*) *Two electrons in a 2s volume.*

(*c*) *Two electrons in one of* $2p_x$, $2p_y$ *or* $2p_z$ *and one electron in each of the others.*

For further description see above.

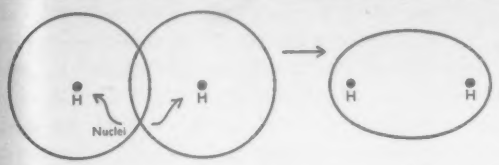


FIGURE 3 – *The* H–H *bond.*

(*a*) *Electron volumes for a pair of isolated hydrogen atoms.*
(*b*) *Electron volumes for a hydrogen molecule. Two electrons in an orbit* (*b*) *comprise the* H–H *bond.*

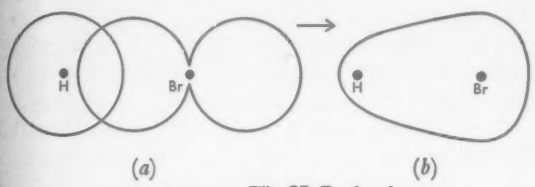


FIGURE 4 – *The* H–Br *bond.*

(*a*) *Electron volumes for isolated hydrogen and bromine atoms.*
(*b*) *Electron volumes for* H–Br *bond electrons. Two electrons in an orbit* (*b*) *comprise the* H–Br *bond.*

that of an atomic electron. The first important characteristic, originally noted by G. N. Lewis in 1916, is that it requires two electrons to establish a single bond between two atoms, as in H_2 or HCl, and four electrons for a double bond, as in O_2. The exceptions to this rule, which are called the 'odd molecules,' such as NO, are odd in more senses than one, and need not be considered in a preliminary account of the theory of chemical binding. The second characteristic is that electrons not involved in the formation of a bond have distinguishing patterns almost identical with those in isolated atoms. When describing the orbits of electrons in molecules, therefore, we need concern ourselves only with those electrons which actually form the bond. These orbits will be similar in general terms to the atomic patterns, except of course that they include two nuclei and may be called bicentric. They are to be interpreted as meaning that although we cannot precisely define the position of these valency electrons, each one is, for practical purposes, effectively confined within a certain contour whose shape may be determined mathematically. Figure 3 (b) shows the contour for molecular hydrogen (H_2), from which we see that the H–H bond is due to two electrons whose orbits distribute them fairly uniformly within a symmetrical sausage-shaped volume. This figure also shows how closely the molecular pattern may be regarded as compounded out of the separate isolated atomic patterns shown on the left. Figure 4 shows how the bond in HBr derives from a molecular pattern composed of a hydrogen 1*s* pattern (as in figure 1) and a bromine 4*p* pattern somewhat similar to that shown in figure 2 for oxygen. Once again the molecular pattern is symmetrical around the axis of the bond, though now, on account of the greater electron-attracting power of the bromine atom, it leans over more to the bromine end of the bond. Two electrons in a bond pattern such as figure 3 or 4 are said to be paired together; in quantum-mechanical language they have their spins opposed to one another. Together they may be said to form an electron-pair bond.

With polyatomic molecules a similar situation occurs. Each bond is formed by two electrons, which are paired together. These each have a pattern which embraces two atomic centres and is closely equivalent to a combination of atomic patterns from the two atoms concerned. The atomic orbits which are thus synthesized into a molecular orbit are always those which overlap one another as much as possible. This, though there is no space to elaborate it here, is really the basis of the theory of valency, and enables us to predict the characteristic valency angles of stereochemistry. Figure 5 shows how the two O–H bonds in water (H_2O) are approximately at right angles, and how they are formed by synthesis of a hydrogen 1*s* pattern and an oxygen 2*p* pattern.

This brings us to resonance itself. As a rule,

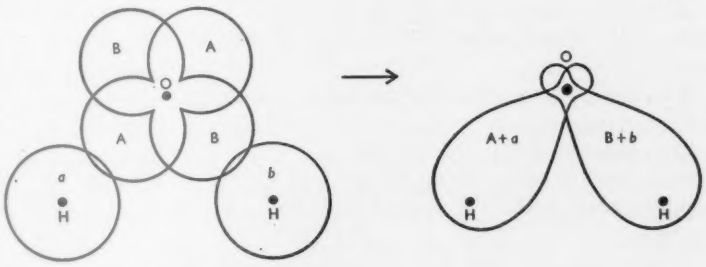
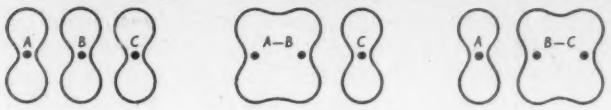


FIGURE 5 – *The water molecule.*

(*a*) *The separate atomic electron patterns.*
(*b*) *The molecular electron patterns.*
Two electrons in each pattern $A + a$ *and* $B + b$ *give rise to the two* O–H *bonds.*



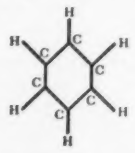
(*a*) (*b*) (*c*)

FIGURE 6

(*a*) *Three isolated unpaired atomic patterns.*
(*b*), (*c*) *Alternative pairings to form molecular patterns.*

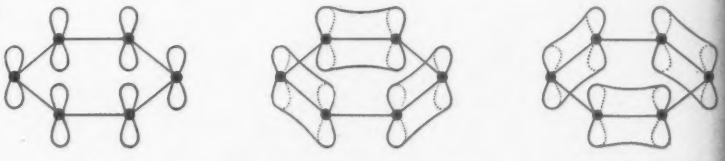
there is no difficulty in saying how the atomic patterns are combined to form molecular patterns localized between two nuclei and giving rise, if there are two electrons concerned, to a normal single bond, and if there are four electrons, to a normal double bond. The criterion that the component atomic patterns are to overlap as much as possible is a sufficient guide. For example, in figure 5 it would be illogical to combine the oxygen pattern *A* with the hydrogen pattern *b*, since the two patterns scarcely overlap at all, whereas oxygen *A* and hydrogen *a* do overlap fairly considerably. But there are occasions when this combining together of atomic orbits is not so unequivocal. For suppose (figure 6*a*) that we have three atomic 2*p* patterns (dumb-bell orbits *A*, *B*, *C*) on adjacent atoms, and that the three patterns are similar and parallel, and point perpendicularly to the line of atomic centres. We are to make molecular patterns from these three atomic ones. Clearly one way is to link *A* and *B* and so make a molecular pattern such as figure 6*b*, in which *C* is left just as in an isolated atom. But equally clearly there is another alternative (figure 6*c*), where we link *B* and *C* and leave *A* isolated. Nobody can say that one of these is favoured rather than the other. In a word, the two possibilities (*b*) and (*c*), which Pauling calls Valence-Bond Structures, are both equally possible: there is no unique pairing of the atomic electrons.

An extreme case—indeed, the *locus classicus* of the phenomenon—occurs in benzene (C_6H_6). This molecule is known to be planar and in the shape of a regular hexagon, thus:



A pair of electrons is allotted to a sausage-like pattern between all adjacent C–C atoms and between all C–H atoms, thus forming a total of twelve normal single bonds. There still remain the six dumb-bell patterns for an atomic electron around each carbon nucleus. These are shown schematically in figure 7*a*. Now, there are obviously two quite distinct ways of joining these in pairs: in a manner exactly equivalent to that illustrated in 6*b* and 6*c* we obtain the molecular patterns 7*b* and 7*c*. Once again there is no unique way of pairing the atomic electrons, for 7*b* and 7*c* are obviously on an entirely equal footing. The mathematical reasoning of quantum theory now tells us that neither of the two structures 7*b*, 7*c* is by itself a valid representation of the appropriate Schrödinger wave function, but a good approximation is obtained if we suppose that both structures contribute equally to a so-called resonance hybrid. Physically this means that benzene should behave partly as if the double bonds were in the one position and partly as if in the other.

But notice what our mathematics implies. For the two structures 7*b*, 7*c* are precisely what Kekulé introduced as long ago as 1865; and he supposed them to be in dynamic oscillation, interconversion taking place too quickly to be observed. Now we see that the phenomenon described as resonance means that instead of two structures alternating rapidly, we must regard the true situation as a simultaneous superposition of both. The bonds do not alternate between single and double: they are at the same time partly single and partly double, according to the way the electrons are paired. Our mathematics has taken Kekulé's original brilliant intuition and fitted it into a formal, logical, and precise theory. An interesting verification of this point of view is given by the carbon–carbon bond length. On Kekulé's picture this would alternate between 1·54 Ångstroms (single C–C bond) and 1·34 Ångstroms (double C = C bond). According to the resonance theory, in which all bonds are equivalent, it should have



(*a*) (*b*) (*c*)

FIGURE 7 – *Benzene pairings.*

(*a*) *Separate unpaired electron patterns.*
(*b*), (*c*) *Distinct alternative pairings to form molecular patterns.*

one distinct length between these two. X-ray measurements show it to be about 1·39 Ångstroms.

Before going any farther we can now give a more inclusive definition of quantum-mechanical resonance. 'When the electrons in a molecule may be paired together in two or more structures which are equivalent or nearly equivalent to one another, the actual molecule does not conform to any one of the structures, but is a resonance hybrid of them all, showing at the same time characteristics of each separate structure.'

Why is it called resonance? Historically the name derives originally from the acoustic phenomenon. Resonance can be illustrated mechanically by the familiar physical experiment in which two simple pendulums of nearly equal lengths are swinging side by side suspended from the same taut horizontal wire. If the two natural periods are nearly equal, it is well known that the two separate oscillations interact and are replaced by two combined modes (normal modes) of vibration, in which the energy flows from one pendulum to the other, so that the amplitude of the one decreases while that of the other increases, and then vice versa. The parallel with benzene is very obvious. Each separate pendulum oscillation corresponds to a particular pairing scheme 7*b* or 7*c* which interchanges with the other. In fact, there is a further important comparison, for there are two possible normal modes for the pendulums. One frequency is greater and the other is less than that of the two components. In the case of benzene there are two ways of superposing the structures 7*b* and 7*c*: one has a lower energy than either structure by itself; the other has a greater energy. We call the resonance hybrid with lower energy the ground state, and the lowering of energy as a result of the superposition of the separate structures is called the resonance energy. Other things being equal, the resonance energy is greater the more structures there are combining. In the case of benzene the upper state is important in absorption of light, and the characteristic appearance of the compound is related to the emission or absorption of light when a quantum jump takes place from the one resonance hybrid to the other.

All this is quite general. On the one hand, there is always a lowering of energy as a result of resonance mixing, which nicely accounts for the relatively great stability of compounds like benzene. On the other hand, this is achieved by delocalizing the electrons. In the case of benzene, on account of the superposition of 7*b* and 7*c* an electron originally round atom No. 1 is sometimes paired in a molecular orbit round atom No. 2, so that it can migrate to this atom. In the new position it may be paired with an orbit from atom No. 3, and may thus continue its migration round the carbon ring. Indeed, we might describe the situation by saying that there are six electrons in benzene which are able to flow as tiny currents round the central hexagon. These currents should show characteristic magnetic effects. Without describing them in detail it may be said that these are just what are found experimentally in the diamagnetic anisotropy. This delocalizing of electrons should also mean that any chemical disturbance at one part of the ring should be propagated (with perhaps a diminishing power) to all other parts of the molecule. This is, in fact, the basis of the theoretical explanation of all the inductive and mesomeric effects so fully investigated by experiments in which one atom or group is replaced by another.

These are important applications of the theory of resonance, but they by no means exhaust its utility. There is space briefly to list five others, in which we choose particular examples to illustrate general principles.

FRACTIONAL BOND ORDER; EXAMPLE, NAPHTHALENE

In benzene there are only two important structures. In naphthalene, however, there are three, as shown in figure 8, corresponding to the three different ways of pairing the atomic electron patterns. If all three of these contribute equally to

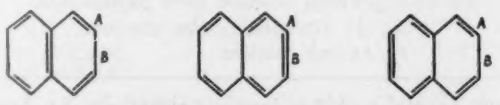


FIGURE 8 – *Three valency bond structures for naphthalene.*

the resonance hybrid (this is not quite accurate, but it is not far wrong), a bond such as that marked *A* would be a double bond for ⅔ of the time and a single bond for ⅓. More accurately, it would be described as ⅔ of a double bond and ⅓ of a single bond. We might call its order 1⅔. Similarly the bond *B* should have an order 1⅓. Clearly *A* would be more similar to a double bond. This fits very satisfactorily with the experimental fact that *A* is more reactive than *B*. But notice that we are now able to assign a numerical (fractional) order to a bond. One result of resonance is to destroy the pure single-bond or pure double-bond

character of a bond and to replace it by a fractional bond order.

IONIC STRUCTURES: EXAMPLE, THE CARBONYL GROUP

Sometimes resonance is confined to a part of a larger molecule. Thus, if R stands for some large saturated radical (in which resonance is not a very significant factor), the molecule R·COOH is an acid; in solution H^+ separates off, leaving a structure that might be represented by the diagram R–C$\langle^{O}_{O^-}$, in which a free electron is found on the one O atom. But another pairing system would lead to the structure R–C$\langle^{O^-}_{O}$. These are called ionic structures to distinguish them from the previous covalent structures. Evidently there is resonance between the two ionic structures. The resulting resonance energy is one strong reason for the acidic property of the original molecule, for it makes the removal of the H atom (without its electron) relatively easy.

METALLIC CONDUCTIVITY: EXAMPLE, A GRAPHITE LAYER

We have just seen how ionic structures contribute to resonance. Their existence also explains

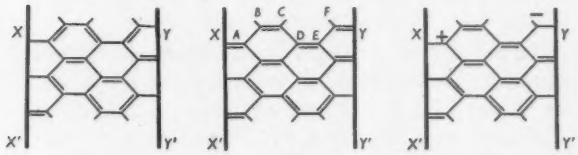


FIGURE 9 – *Bond structures for a graphite layer. (a), (b) Alternative covalent structures. (c) An ionic structure.*

how a metal is able to conduct electricity, i.e. how electrons can move with greater or less freedom over a regular lattice of atoms. Consider in particular a small element $AB \ldots F$ of a layer of graphite, shown in figure 9, in which the carbon atoms are arranged in a regular hexagonal array and which is bounded by the electrodes of a battery at XX' and YY'. We can draw a series of resonance structures to illustrate the pairings of electrons, just as we have already done for benzene in figure 7. Figures 9*a* and 9*b* are two examples from a very large number. Then on account of the alternative electron pairings represented by 9*a* and 9*b*, an electron originally at X can move first to A, then to $B, \ldots$, and finally to Y. So electrons are able to move quite freely through the lattice. The only difficulty is that, so far, whenever one electron moves in one direction another electron momentarily paired with it must move in the opposite direction, so that there is no net flow of charge. To get such a flow we must introduce ionic structures like 9*c*, in which there is an extra electron on atom F at the expense of atom A. Normally this structure will be balanced by another, with the charges interchanged. But in the presence of a suitable electric field $\mathscr{E}$ will predominate and there is a partial flow of charge. If the electrodes of the battery are able to collect this charge at YY' and re-issue it to the crystal layer at XX', we can understand why the applied e.m.f. is able to cause a steady flow of current. Ohm's law is therefore bound up with the relative importance of ionic structures such as 9*c*.

CHEMICAL REACTIONS: EXAMPLE, $H_2 + Br_2 \rightarrow 2HBr$

Resonance also enables us to understand what is happening in a chemical reaction. Consider the reaction $H_2 + Br_2 \rightarrow 2HBr$. In figure 10*a* we show the H_2 and Br_2 molecules approaching one another in such a way as to facilitate the conversion to two HBr molecules shown in (*e*). The original interpretation of this reaction, due to Erlenmeyer (1901), was that as the H_2 and Br_2 approached, there came a sudden moment when the bonds switched over and instead of H–H and Br–Br we discovered two molecules of H–Br. But now we see that there is no sudden switching of the bonds: there is a gradual transition. In (*b*) the structure $\begin{matrix} H & Br \\ | & | \\ H & Br \end{matrix}$ contributes more than $\begin{matrix} H\text{–}Br \\ H\text{–}Br \end{matrix}$. But in (*c*) they contribute equally to the resonance hybrid. This latter situation is sometimes called

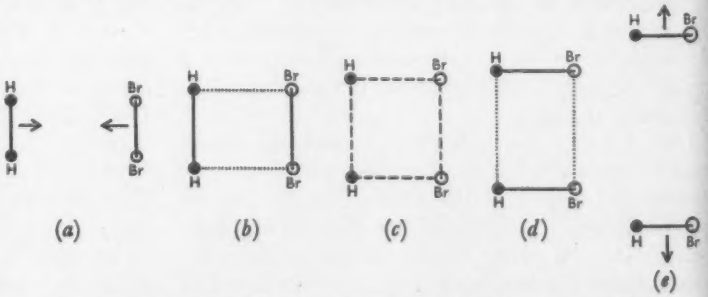


FIGURE 10 – *Successive stages in the reaction* $H_2 + Br_2 \rightarrow 2HBr$.

the Reaction Complex or Activated Complex: in it the bonds are scarcely localized at all. As the reaction proceeds, in (*d*) the $\begin{matrix}\text{H–Br}\\ \text{H–Br}\end{matrix}$ structure is dominant, till finally in (*e*) two H–Br molecules are existing completely in their own right, and the reaction has taken place.

POLYMERIZATION: EXAMPLE, POLYTHENE

A closely similar explanation can be given for polymerization reactions, so important in the study and development of artificial rubber. Below (figure 11) we show the first stage in the polymerization of ethylene to polythene. As two ethylene molecules (C_2H_4) approach together

(I) $H_2C = CH_2$ $H_2C = CH_2$
(II) $- - - H_2C - CH_2 - -$ $- - H_2C - CH_2 - - -$
(III) $- H_2C - CH_2 - CH_2 - CH_2 -$

FIGURE 11 – *Stages in the polymerization of ethylene.*

there is a small amount of resonance between the structure (I), with two localized double bonds, and (II), in which the double bonds have been opened up and pairing takes place across the central carbon atoms. As the molecules approach more closely (II) becomes increasingly important, so that we finish with (III), in which the free valency at either end of the chain makes the subsequent addition of more ethylene units at least as easy as the first.

But enough has been said to show the wide application of the concept of resonance. One last question arises: is resonance a *real* phenomenon? The answer is, quite definitely, no. For consider benzene, with its two Kekulé structures 7*b*, *c*. We cannot say that the molecule has either one or the other structure, or even that it oscillates between them. There is, in fact, simply the C–C aromatic bond. Putting it in mathematical terms, there is just one full, complete, and proper solution of the Schrödinger wave equation that describes the motion of the electrons. Resonance is merely a way of dissecting this solution: or, indeed, since the full solution is too complicated to work out in detail, resonance is one way—and that not the only way—of describing the approximate solution. It is a 'calculus,' if by calculus we mean a method of calculation; but it has no physical reality. It has grown up because chemists have become so used to the idea of localized electron-pair bonds that they are loth to abandon it, and prefer to speak of a superposition of definite structures, each of which contains familiar single or double bonds and can be easily visualized. Like most good things, the idea can be overworked, but no-one can deny that in the years since 1933 it has proved extraordinarily successful in correlating, explaining, and even predicting an astonishingly large and varied body of chemical experience.

Book reviews

FRONTIERS OF ASTRONOMY

Frontiers of Astronomy, *by David S. Evans. Pp.* 174, *with* 8 *plates and* 47 *diagrams. Sigma Books Ltd., London.* 1946. 6*s. net.*

Dr Evans has achieved a considerable measure of success in the difficult task of endeavouring to explain in simple terms, which the general reader can understand, some of the problems with which astronomers are concerned today and why solutions to these problems are required. In a slender book, such as this, it is possible to deal only with selected topics and the particular choice of topics is naturally conditioned to some extent by the personal interests of the author. It is therefore perhaps ungenerous to criticize the choice of subject matter. Reference might have been made to some of the unsolved problems of the solar system. It is true that the centre of gravity of astronomical research has moved away from the solar system (the sun excepted), and the reader may conclude that there is nothing more to be learnt. But the problems of the origin of comets, of the nature of the clouds of Venus, of why Venus has no water while the earth has plenty, of the nature of the markings on Jupiter and of the colours of its belts, of the sudden brightening and fading of certain comets, all need solutions and are but a few of the problems of the solar system. The sun's corona is now being intensively studied and undoubtedly holds the key to many solar problems; more might have been said about this and about the magnetic fields of sunspots, which are invariably involved in the production of solar flares. The fact that no mention is made of astronomical investigation by radio and radar — electromagnetic radiation from the sun and the Milky Way giving rise to radio noise, radar reflections from meteors, etc.—is merely a reminder that astronomy advances so fast that any book dealing with its frontiers is necessarily somewhat out of date before it leaves the publishers.

H. SPENCER JONES

DIFFRACTION BY MOLECULES

The Diffraction of X-rays and Electrons by Molecules, *by M. H. Pirenne, with a foreword by P. Debye. Pp. xii + 160. Cambridge University Press.* 1946. 12*s.* 6*d. net.*

This book deals chiefly with the theory of the diffraction of X-rays and electrons by atoms and molecules, and the use of diffraction methods for the determination of the geometry of simple gas molecules. It is a book about physical principles and methods rather than results. The exposition is admirably clear and concise, and the subject matter will interest not only specialists in the subject but also a wider circle of readers. All X-ray diffraction workers, for instance, will find very useful the earlier chapters on coherent and incoherent scattering, fluorescent radiation, and atomic scattering factors for X-rays; the general reader will be grateful for the discussion of the relative merits of X-ray and electron diffraction methods for studying gas molecules, and will, it is to be hoped, agree with the author's conclusion that both methods should be used for certain types of molecules. If one suggestion may be offered it is this. In Dr Pirenne's book, much less space is given to electron than to X-ray diffraction, although in fact it is the electron method that has been the more widely used of the two for the study of gas molecules. This preferential treatment of X-rays is understandable, because X-ray diffraction is the author's own field of original work, but the book would be better balanced, and would fulfil more adequately the expectations aroused by its title, if the two subjects were treated on an equal footing. Perhaps, however, one should not question a writer's scope, but only sympathize with his difficulty in finding a suitable title for his work. Altogether, this book is a very welcome addition to the literature of diffraction methods.

C. W. BUNN

SCIENCE AND NUTRITION

Science and Nutrition, *by A. L. Bacharach. Pp.* 142. *C. A. Watts & Co. Ltd., London. Second edition,* 1945. 5*s. net.*

The second edition of this book should be as popular as the first. The author has undoubtedly fulfilled his purpose of putting before the reader an account of the methods used in the laboratory for exploring nutritional problems and of the knowledge thereby obtained. He has done it with a simplicity of phrase and use of apt simile that facilitate assimilation. Nowhere does his intention to treat nutrition from the standpoint of the chemist cause him to overlook the nutritional value of substances, even if their chemical complexity be that of the essential oils.

This edition adopts the well-planned arrangement of the first, and incorporates much new material. After a brief account of the form of animal experimentation is a description of the basic constituents of diet: the proteins, fats, and carbohydrates. Two more sections deal with minerals and vitamins. The subject matter is chosen with care and includes only such recent findings upon amino acids, trace elements, and newly isolated vitamins as can be accepted without doubt.

In applying to man the results obtained with laboratory animals the author emphasizes the need for caution. Yet they do suggest that malnutrition in man can arise from a multitude of causes and can be responsible for as much ill-health as infection. As a remedy the author describes in the last section of his book an optimal diet, in the design of which he has combined commonsense with laboratory results; he advocates that all should have the means to obtain it. His book should provide that instruction upon nutrition which will ensure that the means are wisely spent.

J. R. P. O'BRIEN

PRACTICAL CHEMISTRY

Practical Chemistry for Medical Students, *by William Klyne. With a foreword by Professor G. F. Marrian. Pp. xvi +* 460. *E. & S. Livingstone Ltd., Edinburgh.* 1946. 20*s. net.*

It has now become recognized that the education of the future physician must be based on a sound scientific background, particularly as regards chemistry. Within the 460 pages of this excellent book, the author has provided an experimental course of study of an ample and varied character. The book is divided into five parts entitled: Some Fundamental Scientific Ideas, Practical Methods, General and Physical Chemistry, Inorganic Chemistry, and Organic Chemistry. In his preface the author emphasizes that the time allotted to chemistry at Edinburgh does not provide for more than half of the work in the book to be covered. One can only remark that so long as the right choice is made, the interest of the student are amply safeguarded.

Great care has been taken to ensure that the student shall approach his experimental work in the right spirit, not only as regards understanding of theoretical principles, but from the standpoint of care and exactness in carrying it out. But the reviewer is inclined to wonder whether the elaborate list of directions on pages 23–25 concerning what is and what is not to be done in matters of manipulation could not have been entrusted to demonstrators. Criticism may be directed to some features of the chapter on volumetric analysis, e.g. titration values of less than 10 ml. on page 132, and the omission of the use of adsorption indicators. On page 424 the author refers to Gerhardt's test for aceto-acetic acid. Presumably he means Geuther's test, since Gerhardt died in 1856, and aceto-acetic ester was discovered by Geuther in 1863.

A. J. BERRY

RELIGION AND SCIENCE

The Fourfold Vision, *by F. Sherwood Taylor. Pp.* 108. *Chapman & Hall Limited, London.* 1945. 6*s. net.*

Dr Sherwood Taylor sets out to show that the knowledge and methods of science are not contrary to religion but may indeed contribute thereto. It is an attempt that has been made by many others, with varying degrees of success, but the present essay is devised especially for the scientist, and largely neglects metaphysical arguments familiar to the philosopher and theologian. The main thesis, from which the book takes its title, is that man can achieve four means of apprehension of nature of which the scientific is but one: first the mere apprehension of diversity without unity; then the perception of the beautiful in nature and its integration in art; next the discovery of harmony in the order of nature through science and philosophy; and finally the apprehension of the world as unified in its orientation to God. Dr Taylor marshals his arguments with great skill and will carry his readers along with him for a certain distance—indeed a considerable distance. But the central problem is perhaps of its nature insoluble, and one cannot help feeling that the book will strengthen the conviction of those already convinced rather than convince those who are not.

Notes on contributors

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D.Sc., F.R.S.,

Is Regius Professor of Zoology in the University of Glasgow and was previously (1933–44) Professor of Zoology in the University of Bristol. He was born in 1899 and was educated at Silcoates School, Wakefield, and at Edinburgh University. After a period of research work he became, in 1925, Assistant Naturalist at the Marine Biological Association, Plymouth, and two years later went to Cambridge as Balfour Student. In 1928 he led the Great Barrier Reef Expedition to Australia. He has worked at many marine laboratories along the Atlantic and Mediterranean coasts of Europe, on both coasts of North America, in the Gulf of Mexico, and at Honolulu. He is Chairman of the Executive Committee of the Scottish Marine Biological Association, and a member of the Advisory Committee on Fishing Research to the Development Commission, and of the Water Pollution Research Board.

JEAN TIMMERMANS,
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